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RADIATION AND ABSORPTION

By W. J. HUMPHREYS

INTRODUCTION

The author has often had weary hunts, through the voluminous literature on the subject, for known facts in regard to radiation and absorption; and many others, doubtless, have had the same sort of time-wasting experience. Perhaps, therefore, the following brief discussion of certain of the more important radiation and absorption phenomena, though containing but little that is new, may be of some use.

A similar article, differing decidedly from the present one, both in scope and method of treatment, and with meteorological applications, will, because of these applications, appear in the *Mount Weather Bulletin*, 2, 109-132. The circulation, however, of this bulletin overlaps but slightly that of the *Astrophysical Journal*, and, as the readers of the latter often are especially interested in the subjects here discussed, it may be worth while to place a modified and more comprehensive article at their service.

GENERAL REMARKS

Everyday experience tells us that a cold object in the neighborhood of a hot one becomes warm, and experiment shows that the same phenomenon can happen when either or both are in as complete a vacuum as can be obtained. The hot object, we say, loses heat by radiation, and the cold one absorbs radiation and becomes warmer; but it is not at all clear how these things are brought about.

We are not yet able to follow, in all its details, the cycle of changes involved in the transformation of molecular kinetic energy into energy of radiation, and this in turn back to molecular kinetic energy. We do not understand, in the sense that we should like to, either cooling by radiation or warming by absorption.

But no matter what the real mechanism of radiation or of absorption, or by what process temperature is modified by these phenomena, they act, in many cases, according to known laws, some of which are general and only qualitative, while others are definite and quantitative. But before outlining the experiments and arguments that led to and justify the formulating of laws, it will be convenient to consider the different known processes of radiation and see to which these laws apply.

CLASSIFICATION

Radiation is often classified, according to its action on the eye, as *luminous* and *non-luminous*; or, according partly to its position in the spectrum as formed by a glass prism, and partly to the sensation aroused in those of normal vision, as *ultra-violet*, *violet*, *blue*, *green*, and so on through the so-called primary colors, and, finally, *ultra-* or *infra-red*.

Both these methods of classification serve useful ends, but are inadequate when minute subdivision is required. For this purpose *wave-lengths* and *wave-frequencies* are used; the former commonly being the more convenient, and the latter often the more valuable of the two.

If now we consider, not the radiation itself, but the processes by which it is produced, we shall find that these fall into two distinct classes, namely:

1. *Incandescence*.—Whenever an object radiates continuously the same way, so long as its temperature is kept constant, we say that the source of the radiant energy is *incandescence*, or that the process by which it is emitted is *pure temperature radiation*. It is excellently represented by a carbon filament when electrically heated *in vacuo*.

2. *Luminescence*.—Whenever the radiation given out by an object changes while the temperature is kept constant, and whenever the intensity of the radiation in any spectral region, however narrow or extended, is greater than that in the same region of an ideally black

body at the same temperature, we call the process by which any excess of radiation is produced *luminescence*. Here the energy flux is not maintained wholly by the heat of the object concerned, but, in part, in some cases almost entirely, by some other of its supplies of energy, and is therefore accompanied by a molecular or other internal change.

Luminescence, in turn, may be subdivided according to its more or less obvious causes. Thus we have:

a) *Chemi-luminescence*.—Illustrated by phosphorescent bacteria, by the firefly, the glow-worm, and the like, where the exciting cause apparently is some sort of chemical change, the nature of which is not understood. Also illustrated by slowly oxidizing phosphorus, where, though the chemical action is well understood, the details of the process by which the object becomes luminescent are still unknown.

b) *Photo-luminescence*.—Divisible into (1) *fluorescence*, as beautifully illustrated by the glow of sodium vapor while excited by radiation of any one or more of certain wave-lengths; (2) *phosphorescence*, as illustrated by Balmain's luminous paint (calcium sulphide), which glows for hours after an exposure to any intense ordinary light. Fluorescence appears to end, like simple reflection, immediately the incident energy is arrested. Still, it is not a reflection phenomenon, and probably does last through an interval of time, however brief. Phosphorescence, on the other hand, continues of itself, like a pendulum set swinging, for a measurable length of time after the initiating disturbance has ceased to act. Both phenomena evidently are due to some effect of absorption other than mere temperature change, perhaps chemical in its nature. Probably, too, they mainly differ from each other only in their durations after the exciting radiation has been shut off.

If X-rays consist, as we believe, of abrupt ether-pulses, then the luminescence excited by them may also be included in this class.

c) *Electro-luminescence*.—Good examples of this are seen in the glows of electrodeless tubes; in barometer stems, sometimes, when the mercury is made to oscillate up and down, and even in electric light bulbs when properly excited. Probably under this head should be classed all radiation due directly to electric discharges, such as the faint glow along the path of cathode rays, the glow excited in many

objects when used as cathode targets, the light of the Geissler tube, of St. Elmo's fire, and of auroras—presumably. Also the steady glow excited in many substances by radium may belong to this class.

d) *Mechanical, or tribo-luminescence*.—Luminescence of this origin usually is faint. It may be produced by the cutting of glass, by the rubbing together of quartz, by the crushing of lump sugar, and by many other processes, such as freezing, crystallization, bombardment by α particles, and the like, all of which, possibly, give but varieties of electro-luminescence.

e) *Thermo-luminescence*.—In this case temperature, apparently, serves only the purpose of setting free some form of stored-up or potential energy. Fluor-spars and diamonds are among the best-known objects that are thermo-luminescent, and these differ greatly in the kind and quantity of the light they emit, and the temperatures at which they become active. Thus the chlorophane (fluor-spar that emits essentially a pure green light) found at Amelia Court House, Va., becomes luminescent on being held for a few moments in the hand, while that from some other localities remains inactive even at the temperature of boiling water.

f) *Cometary luminescence*.—This term is used here to apply to the light phenomena of comets' tails, and, perhaps, also of nebulae. Possibly this too is a case of electro-luminescence, but as yet no one knows, and therefore the new name is suggested as a means of stating briefly, but unequivocally, that we know nothing, or next to nothing, about the real process by which the tails of comets become luminous.

In regard to all classes of luminescence our information is extremely fragmentary. In fact it is only that radiation which is due entirely to incandescence, of whose quantity and spectral distribution we have knowledge sufficiently extensive and exact to formulate into laws. Nor does this knowledge extend, even approximately, to the thermal radiation of all substances, nor are the quantitative laws applicable except to specially devised and artificially constructed bodies, and to substances with ideal properties. Nevertheless, in spite of the excessive difficulty of the subject, a great deal of labor, both on experiment and on theory, has been given to radiation and absorption; and the following few laws are of the greatest value, not only in pure physics, but also in many of the arts as well.

It must not be overlooked, however, that the lights themselves of different luminescent origins obey the same laws as does that due to incandescence. They are indistinguishable, when the examination is confined to any single wave-length, each from any other, and doubtless are all due to internal or ionic disturbances, no matter how different may be the methods, thermal, electrical, chemical, or what not, of initiating and maintaining these disturbances.

CONTINUOUS EXCHANGE—PREVOST'S LAW

More than a century ago Prevost¹ advanced the theory, substantiated by every known test, that any two objects, when there is no intercepting medium between them, continue to radiate and, to some extent, mutually to absorb each other's radiation, whatever their temperatures. According to this well-substantiated theory any object, no matter how cold, supplies some heat to its neighbor, no matter how hot.

This means, (1) that an object continues to radiate to a greater or less extent, whatever its temperature; and (2) that no supply of heat can render it either completely diathermanous, or a perfect reflector. It therefore continues to give out energy by radiation, and at the same time to absorb a part, at least, of any radiant energy that may be incident upon it, so that partial energy exchange must take place between objects unscreened from each other, regardless of either equality or inequality of their temperatures.

A valuable application of this law of exchanges is found in the use of a pyrheliometer. The readings of this instrument depend in part upon its own temperature before exposure, as well as upon that of the object whose radiation and temperature are being determined.

As will be more fully explained later, we can write

$$R = CT^n,$$

in which R is the total radiation per second per unit area of any given object, C a constant, peculiar to the substance of the object in question, T the absolute temperature, and n a number which, in the case of the full radiator, or black body, is 4. Then, if G is the amount of heat gained per second per unit area by the pyrheliometer

¹ *Sur l'équilibre du feu*, Genève, 1792; *Du calorique rayonnant*, Genève, 1809.

receiver, we have, in the case of no intervening absorbing medium, and no other contributing radiator,

$$G = \omega_1 C_1 T_1^{n_1} - \omega_2 C_2 T_2^{n_2},$$

in which T_1 is the absolute temperature of the object under consideration, C_1 and n_1 its radiation constant and exponent; T_2 , C_2 , and n_2 the corresponding pyrliometer values, and, finally, ω_1 and ω_2 the solid angles subtended at the receiver by the radiator and the bolometer opening respectively.

This assumes absolutely no loss of heat from the receiver except by radiation through the pyrliometer opening, an assumption that, in practice, would be difficult to realize even approximately. A more practicable equation is

$$G = \omega_1 C_1 T_1^{n_1} - \omega_2 C_2 T_2^{n_2} - H,$$

in which H is the heat lost by methods other than radiation from the receiver, controllable, by fixing the value of T_2 , and accurately measurable.

UPON WHAT THE RADIATION AND ABSORPTION OF AN OBJECT DEPENDS

The amount of energy emitted by incandescence per second per unit area (smooth) of an object depends upon its composition, its temperature, and the refractive index of the surrounding medium, and not in any way upon the temperatures, compositions, or positions of neighboring objects; while the energy absorbed depends upon the composition of the absorbing surface and also upon the amount and quality of the incident energy, that is, upon the compositions, temperatures, and angular sizes, as viewed from the absorber, of surrounding objects.

As surfaces are ordinarily measured it is necessary to consider their physical state. A mat surface radiates and absorbs more than does a smooth one, because of multiple reflections within the minute cavities and its consequent approach to a full radiator, or ideally black body.

TWO RELATIONS, QUALITATIVE AND QUANTITATIVE

It must be clearly kept in mind, as Cotton¹ has emphasized, that there are two distinct relations between radiation and absorption, one

¹ *Astrophysical Journal*, 9, 237, 1899.

merely qualitative, the other quantitative, that often are confused. The qualitative relation deals with the radiation and absorption of a single object under ordinary but not necessarily clearly defined conditions, while the quantitative relation is that which exists between the radiation and absorption, properly defined, of two different bodies at the same temperature, one of them at least being a full radiator and perfect absorber. It shows how this relation, which is the same for all bodies, varies with temperature and is related to wave-length.

Whenever any object is emitting radiations of a given wave-length and polarization, it will absorb identical radiations coming to it from without. But, in many cases at least, absorption is not confined to the kind of radiation emitted. Nearly all objects, even some of the most transparent, such as water and glass, absorb ultra-violet radiations at ordinary temperatures; though at these temperatures they emit them so feebly, if at all, that they have never been detected. Similarly, colored objects absorb radiations, which, at room temperatures, there is no evidence of their emitting. Although carbon dioxide, water vapor, and some other substances, when cold, absorb lines and bands which at higher temperatures they appreciably emit, still there is no certainty that this property is universally true, nor are we aware of any quantitative relations between temperature, absorption, and emission in even the best-known of these cases. All that can safely be said, in this connection, is that good absorbers are good radiators, and that good radiators are good absorbers; but it must be distinctly understood that these are only qualitative rules.

RADIATION WITHIN A CLOSED EQUAL-TEMPERATURE SHELL

Let a shell of any shape and material whatever be at a uniform temperature and have an adiathermanous outer surface so that all its heat must be retained—a polished silver surface would approach these ideal conditions. Now let a flexible tube with parallel walls that are perfectly reflecting within and without be placed within the shell, and let the ends of this exploring tube be located and oriented at random. Radiation will stream through it from both ends, and if it is more intense in one direction than in the other, then the heat energy will assume a new distribution on the shell, and the second

law of thermodynamics will be violated, inasmuch as heat, in excess of mutual exchange, will be transferred, without the aid of external work, from an object at one temperature to another at the same or even a higher temperature.

We conclude, therefore, that the radiation within a closed equal-temperature shell is of the same intensity throughout the inclosed space, and in every direction.

Now let the tube be crossed by a partition such that only radiation of a certain type of polarization, or of a certain limited range of wave-length, or of both, can get through. Again, if the second law of thermodynamics is not to be violated, the energy flux must be the same in both directions, and we add to equality of intensity equality of kind of radiation at every place and direction within an inclosure whose walls are in thermal equilibrium throughout. We say that radiation in such a space is perfectly diffused.

Even if the walls of the shell be made of different materials, of one thing at one place and of something else at another, still, if the second law of thermodynamics is to hold, there must obtain, under all such conditions, equality of intensity and kind of radiation at every point within the inclosure, and in every direction. That is to say, when two objects are in thermal equilibrium, each with the other, the radiation emitted by the first and absorbed by the second agrees in every particular, heating effect, intensity, wave-length, and polarization, with that emitted by the second and absorbed by the first.

To determine just what kind of radiation fills an inclosed cavity let a portion of the inner wall be made of a perfect absorber, or an ideally black body. Such material reflects no radiation of any kind, and therefore radiation directed *away* from it must be entirely its own radiation. Hence a closed shell, whose inner walls are in thermal equilibrium with each other, is filled with radiation that everywhere, and in every direction, is identical, both in intensity and in kind, with that from the surface of an ideally black body at precisely the same temperature and surrounded by a medium of the same refractive index as that which fills the shell. The reason for this last condition, involving the refractive index of the adjacent medium, will be seen later.

Since the inner walls of the shell may consist in part or wholly

of materials selectively reflective, that is, of materials that reflect radiation of certain wave-lengths better than that of others, and since the radiation that fills the shell still is of the black body type, it therefore follows that those spectral regions which a substance reflects well it radiates poorly, while those it absorbs it correspondingly radiates, when at the proper temperature. Similarly, those radiations a substance transmits well it radiates but feebly. Also, inasmuch as an object of any kind within a constant-temperature shell does not disturb the perfectly diffused condition of the radiation, therefore the radiation, e_θ , emitted by any object at the angle θ from the normal is equal to the radiation, a_θ , absorbed by this object at the same angle, or $e_\theta = a_\theta$ for all angles, when the object is in thermal equilibrium with its surroundings.

COSINE LAW—LAW OF LAMBERT

By observation and by experiment we know that radiation moves in straight lines through a medium whose refractive index is constant. Therefore within a shell of constant temperature, where the radiation is perfectly diffused, the amount of radiation parallel to the sides of a straight-walled tube of constant cross-section is the same throughout its length and independent of the direction along which it lies.

Let one side of the shell be flat, and let the tube point first to one and then to another part of this flat portion. Let the angle between the normal to this surface and the axis of the tube be θ_1 in the first position, and θ_2 in the second, and let A be the cross-section of the tube. Also let e be the radiation per second per unit area normal to the flat surface, and $e\psi(\theta)$ its radiation per second per unit area at an angle θ from the normal.

The areas that contribute radiation parallel to the walls of the tube, in its two positions, are $\frac{A}{\cos \theta_1}$ and $\frac{A}{\cos \theta_2}$, respectively. But the total amount of this radiation is the same in the one case as in the other; therefore

$$\frac{A}{\cos \theta_1} e\psi(\theta_1) = \frac{A}{\cos \theta_2} e\psi(\theta_2),$$

or

$$\frac{\psi(\theta_1)}{\cos \theta_1} = \frac{\psi(\theta_2)}{\cos \theta_2}.$$

But θ_1 and θ_2 have any values from 0 to $\frac{\pi}{2}$, and, besides, when $\theta_1 = 0$, $e\psi(\theta_1) = e$, or $\psi(\theta_1) = 1$.

Hence, in this case

$$\psi(\theta_2) = \cos \theta_2,$$

or, in general,

$$\psi(\theta) = \cos \theta.$$

That is to say, the intensity of the radiation in any direction from a black surface is directly proportional to the cosine of the angle between that direction and the normal to the surface. In the case of objects that are not full radiators the same law, while not exact, applies approximately, since the color and brilliancy of objects remain substantially the same, no matter at what angle they are viewed.

TOTAL RADIATION FROM A BLACK SURFACE

Let $e_\lambda d\lambda$ be the radiation per unit area per second, between λ and $\lambda + d\lambda$, normal to the radiating surface. Then, where θ is the angle between the direction of the radiation and the normal to the surface, we have for the total radiation, of wave-length λ , per second from a flat black surface of area S ,

$$R_\lambda = 2\pi e_\lambda d\lambda S \int_0^{\frac{\pi}{2}} \cos \theta \sin \theta d\theta = \pi e_\lambda d\lambda S,$$

or $\pi e_\lambda d\lambda$ per unit flat area.

This value differs greatly with different wave-lengths. Hence for the total radiation per second per unit flat black area we have

$$R = \pi \int_0^\infty e_\lambda d\lambda.$$

When the temperature of the radiating surface is $1^\circ \text{C. absolute}$, then, by definition, its *total* radiation per second per unit area is its *emissive power*.

STEWART-KIRCHHOFF LAW

Consider a unit flat surface of any material surrounded by walls at the same temperature as that of the inclosed object. As just seen, the total radiation per second of this surface, if black, is

$$R = \pi \int_0^\infty e_\lambda d\lambda.$$

But the temperature of this object remains constant (to change would be to violate the second law of thermodynamics) and as it is black it absorbs all incident radiation. Let H be the amount of radiation incident per second on the given unit area, then $(H)_T = (R)_T$, in which T is the constant temperature under consideration.

If, however, the surface is not black then it will absorb only A units of the total, H , incident, and, during the same time, emit E units. But, as the temperature remains constant, $(E)_T = (A)_T$.

Hence

$$(E)_T = \left(\frac{A}{H} R \right)_T,$$

or

$$\left(\frac{\frac{E}{A}}{\frac{H}{H}} \right)_T = (R)_T.$$

This means that the ratio of the emissivity of any object to its coefficient of absorption (energy absorbed divided by energy incident) depends upon its temperature only; and, numerically, is equal to the emissivity of the full radiator at the same temperature.

By the aid of an inclosing screen, perfectly reflecting to all wavelengths except one, and fully transparent to this, the interchange of radiant energy between the inclosed object and the outer shell can be restricted to a single wave-length, λ , but still the temperature of the inclosed object must remain constant, since otherwise an object at one temperature would be able to warm another to a higher, a result contrary to all experience. Therefore the radiation, $(A_\lambda)_T$, absorbed, must equal the radiation, $(E_\lambda)_T$, simultaneously emitted, and

$$\left(\frac{\frac{E}{A}}{\frac{H}{H}} \right)_{\lambda, T} = (R)_{\lambda, T}.$$

By the introduction of a polarizer in the path of the energy flux, the radiation exchanged can be restricted to any particular azimuth, ϕ , of polarization, so that we can more specifically write

$$\left(\frac{\frac{E}{A}}{\frac{H}{H}} \right)_{\lambda, \phi, T} = (R)_{\lambda, \phi, T}.$$

ENERGY OF RADIATION

Let the motion of a vibrating particle be expressed by the equation

$$y = a \sin(\omega t - a),$$

in which y is the displacement at the time t from the point of rest, a the amplitude, or maximum displacement, $\omega = \frac{2\pi}{\tau}$, in which τ is the time of a complete vibration, a the epoch, or phase at the instant observations began.

The velocity, s , of the displaced particle is given by the equation

$$s = \frac{dy}{dt} = a\omega \cos(\omega t - a).$$

The time of a complete vibration is τ , and therefore the average energy of a vibrating particle of mass m , is

$$\begin{aligned} \frac{1}{\tau} \int_0^\tau \frac{1}{2} m s^2 dt &= \frac{ma^2\omega^2}{4\tau} \int_0^\tau 2 \cos^2(\omega t - a) dt, \\ &= \frac{ma^2\omega^2}{4} = m\pi^2 \frac{a^2}{\tau^2}. \end{aligned}$$

Therefore the average energy is just half the maximum, since the maximum velocity is $a\omega$. Also, on the whole, the energy of the vibrating particle is half potential and half kinetic.

Where the velocity of the wave disturbance is independent of wave-length, as is the case with radiation *in vacuo*, we can write $\frac{\tau'}{\tau} = \frac{\lambda'}{\lambda}$, and therefore, if E_λ is the kinetic energy per unit volume, due to radiations of wave-length λ , we can write $E_\lambda = \rho \pi^2 \frac{a^2}{\lambda^2} c^2$, where ρ is the ether density, and c the velocity of light *in vacuo*.

DOPPLER EFFECT OF A MOVING MIRROR ON RADIATION

Following the method used by Larmor,¹ let radiation, moving with velocity c , meet normally a perfect mirror approaching it with the velocity u . The reflected radiation will be changed in several particulars, among them wave-length. This, in regions where the refractive index is greater than unity, would lead to some complication, so that, in what follows, it will be assumed that $\mu = 1$ for all wave-lengths, or that we are dealing with radiation phenomena

¹ *Encyclopaedia Britannica*, 32, 121.

in vacuo. Let the path of the incident radiation and of the mirror be along the axis x . Let the initial position of the mirror be at $x=0$, and let it move in the positive direction.

The displacement, y , due to the incoming radiation, at any place x and time t is given by the equation

$$y = a \sin \frac{2\pi}{\lambda} (ct + x),$$

in which a is the amplitude and λ the wave-length.

The corresponding disturbance due to the reflected radiation, since c is independent of both wave-length and amplitude, is represented as follows:

$$y' = a' \sin \frac{2\pi}{\lambda'} (ct - x).$$

Since the mirror is a perfect reflector, at its surface $y + y' = 0$ at all times, and therefore also at the point x when $x = ut$. Hence

$$a \sin \frac{2\pi}{\lambda} (ct + ut) + a' \sin \frac{2\pi}{\lambda'} (ct - ut) = 0,$$

whatever the value of u .

Therefore

$$a = -a'$$

and

$$\frac{\lambda'}{\lambda} = \frac{c - u}{c + u}.$$

This means that the reflected and the incident radiations have the same amplitudes, but, at the surface of the reflector, opposite phases; while their wave-lengths are to each other as the difference to the sum of the two velocities concerned.

RADIATION PRESSURE—MAXWELL-BARTOLI EFFECT

That radiation exerts a pressure was deduced theoretically first by Maxwell,¹ and later in a different manner by Bartoli.² Subsequently it was proved experimentally by Lebedew³ and by Nichols and Hull.⁴

¹ *Treatise on Electricity and Magnetism* (first ed.), 2, 391, 1873.

² *Nuovo Cimento*, 15, 193, 1884.

³ *Rapports, Congrès International de Physique*, 2, 133. Paris, 1900.

⁴ *Physical Review*, 13, 293, 1901; *Proc. Am. Acad.*, 38, 559, 1903.

Consider a straight cylinder of unit cross-section with perfectly reflecting walls and ends. Let this be filled with monometric, or single wave-length, radiation, and let one of the ends move in slowly with the velocity u . Let a wave start from the fixed end with the velocity c and, at the end of the time t , reach, at the distance ct , the moving end which, during the same time, has come in a distance ut . It is now reflected, and when it has returned to its starting-point, or completed a cycle, the movable end will have come in an additional distance ut . Therefore the length of the closed cylinder, when the radiation left the fixed end, is to its length at the completion of the cycle as $ct+ut$ is to $ct-ut$. But this, as we have seen, is the ratio of the old to the new wave-lengths, or of λ to λ' .

As the walls are perfectly reflecting no radiation energy can get out, and as amplitude is not changed by reflection, therefore the energy density is increased in the ratio of λ^2 to λ'^2 , or of $(c+u)^2$ to $(c-u)^2$. Therefore, after, and because of, the compression the energy in the inclosure is greater than before, which, from the conservation of energy, proves that work has been done by virtue of volume change. Hence there must be a radiation pressure, such that $dQ = p dV$, where dQ is the change in the total energy of the volume V , and p the average radiation pressure.

The following discussion of radiation pressure on a mirror is essentially that given by Larmor.¹

Let e be the energy density of the normally incident radiation, then, as above seen, the energy density of the reflected radiation is

$$e \left(\frac{c+u}{c-u} \right)^2.$$

If e_λ and $e_{\lambda'}$ are the energies respectively per incident and per reflected wave-lengths, then

$$\frac{e_{\lambda'}}{e_\lambda} = \frac{c+u}{c-u}.$$

The number of waves incident per unit of time on the reflector is $\frac{c+u}{\lambda}$, and therefore the radiation energy added in the same time,

¹ *Encyclopaedia Britannica*, 32, 121.

by virtue of the moving mirror, is

$$(e_{\lambda'} - e_{\lambda}) \frac{c+u}{\lambda} = pu,$$

the corresponding work done against pressure. Substituting for $e_{\lambda'}$ its value in terms of e_{λ} , we get

$$\left(\frac{2e_{\lambda}u}{c-u} \right) \frac{c+u}{\lambda} = pu.$$

But $\frac{e_{\lambda}}{\lambda} = e$, the energy density of the incident radiation. Therefore we get

$$p = 2e \frac{c+u}{c-u}.$$

The energy density in front of the mirror, including both incident and reflected radiation, is

$$e \left[1 + \left(\frac{c+u}{c-u} \right)^2 \right],$$

or

$$2e \frac{c^2 + u^2}{(c-u)^2}.$$

If we let E represent this total energy density, then

$$p = E \frac{c^2 - u^2}{c^2 + u^2}.$$

The above concerns radiation pressure when the mirror is moving *against* the radiation. If it is moving in the same direction, so as to increase its distance from the source, the signs are reversed. Therefore in general

$$p = 2e \frac{c \pm u}{c \mp u} = E \frac{c^2 \mp u^2}{c^2 \pm u^2},$$

in which the upper signs refer to motion toward the source of radiation, and the lower to motion away from it. When $u = 0$, $p = 2e = E$.

It must not be overlooked that the above concerns only that radiation which is to and fro along a path at *right angles* to a *mirror* that sustains the pressure.

In the case of perfectly diffused radiation, filling a cube, say, whose inner walls are perfectly reflecting, we can resolve the pressure due to the radiation in each direction, normal and parallel to the walls. This will be equivalent to what would be obtained by similarly

resolving the radiation itself, if such a thing were possible. Consequently, in the case of diffuse radiation, acting on a mirror,

$$p_d = \frac{1}{3} E \frac{c \pm u}{c \mp u},$$

E being total radiation density.

When $u=0$, $p_d = \frac{1}{3} E$, in the case of a mirror. If a black surface is used instead of the reflecting mirror, energy is absorbed in it at the rate of $e(c \pm u)$. By moving the absorbing surface a distance l along the path of radiation the amount of energy absorbed, or the amount of energy transferred—work done—is increased, if toward the radiator, or decreased, if in the opposite direction, by el . Therefore, in the case of a perfect absorber, whatever its velocity along the path of radiation, $pl = el$, or $p = e$, in which e is the energy density of the singly directed radiation. Hence radiation pressure on a perfect absorber, being independent of velocity, is analogous to sliding friction. If the radiation is diffused and the absorber is in thermal equilibrium with it, $p = \frac{1}{3} E$, in which E is the energy density of the total radiation. Here half the pressure is the reaction due to the emission by the radiator.

As no known substance is either a perfect absorber or a perfect mirror, radiation pressure, where the distance to the source is constant and the receiver adiathermanous, must be greater numerically than once and less than twice the density of the incident radiation. If the receiver is in part diathermanous, additional complications are introduced.

RELATION OF TOTAL RADIATION OF A BLACK BODY TO ITS TEMPERATURE—STEFAN-BOLTZMANN LAW

This relation was first determined as an empirical law by Stefan¹ from the experiments of others, and later deduced by Boltzmann² from thermodynamic considerations similar to those used by Bartoli in his work on radiation pressure. In what follows, however, Larmor's³ method will be closely followed.

Let $E_\lambda d\lambda$, which we will briefly designate a , be the energy density of diffuse radiation of wave-lengths λ to $\lambda + d\lambda$ within a space whose

¹ *Wien. Akad. Ber.*, **79**, 391, 1879.

² *Wied. Ann.*, **22**, 291, 1884.

³ *Encyclopaedia Britannica*, **32**, 122.

volume is V . Let it be surrounded by perfectly reflecting walls, so that none of the energy can escape, and let the walls be pushed in slightly against the radiation pressure.

Now, remembering that the change in volume is a decrease, that dV is negative, we get, from the conservation of energy,

$$aV - \frac{1}{3}adV = (a+da)(V+dV).$$

Therefore

$$Vda = -\frac{1}{3}adV$$

and a is proportional to $V^{-\frac{1}{3}}$.

If the original radiation density a is in equilibrium with a thermal source at the absolute temperature T , and the new density $a+da$, with some other temperature $T+dT$, then, by Carnot's principle,

$$\frac{aV - \frac{1}{3}adV}{aV} = \frac{T+dT}{T},$$

or T is proportional to $V^{-\frac{1}{3}}$, and T^4 varies as $V^{-\frac{4}{3}}$. But a varies as $V^{-\frac{1}{3}}$.

Therefore $a = KT^4$, K being a constant. That is, $E_\lambda d\lambda$, for every value of λ , is directly proportional to T^4 , or the total radiation, R , per unit of time and surface of a black body at temperature T , may be written as $R = CT^4$.

This furnishes an excellent practical means for determining the temperature of one full radiator in terms of another.

An imperfect radiator, even when losing energy through incandescence only, radiates according to some power of its temperature greater than the fourth, but one that cannot be calculated, or easily determined experimentally, since, in many cases at least, it changes—approaches four, as the temperature increases.

One of the most carefully investigated radiators is polished platinum, which from 400°C . to 1600°C . gives off total radiation at a rate approximately proportional to T^5 .

It must not be supposed, however, that polished platinum or anything else, for that matter, radiates more at a given temperature than does the full radiator whose temperature exponent is only 4. As a matter of fact all such objects radiate less, and thus have smaller values for their temperature coefficients.

RELATION OF WAVE-LENGTH TO TEMPERATURE—WIEN'S
DISPLACEMENT LAW

As just shown, T varies as $V^{-\frac{1}{3}}$. But as compressing the volume inclosed by perfectly reflecting walls decreases the wave-lengths in proportion to the change in their paths, that is to say, changes the wave-lengths without altering the number of inclosed waves, therefore

$$\frac{\lambda_1^3}{\lambda_2^3} = \frac{V_1}{V_2},$$

or

$$\lambda = \lambda_0 V^{\frac{1}{3}},$$

in which λ_0 is the wave-length corresponding to unit volume.

Therefore λT is a constant, or the higher the temperature the shorter the corresponding wave-length.

The equation $\lambda_{max} T = \text{a constant}$, in which λ_{max} is the wave-length of maximum radiation, furnishes a reliable means of determining the temperature of a full radiator.

RELATION OF THE SPECTRUM OF A BLACK BODY TO ITS TEMPERATURE

As already explained, $E_\lambda d\lambda = K T^4$, in which K is a constant.

Also $T\lambda = \text{a constant}$.

Now let λ_1 and λ_2 , of which $\lambda_2 > \lambda_1$, be two wave-lengths of nearly the same value at the temperature T , and λ'_1 and λ'_2 their corresponding values at the temperature T' , then

$$\frac{T(\lambda_2 - \lambda_1)}{T'(\lambda'_2 - \lambda'_1)} = \frac{T\delta\lambda}{T'\delta\lambda'} = 1,$$

or $T\delta\lambda = \text{a constant}$, and therefore E_λ is proportional to T^5 .

If we consider the radiation energy confined to the region between λ and $\lambda + d\lambda$ at any given temperature T , this energy will remain proportional to T^4 , while the width, $d\lambda$, of the spectral region it covers, and its wave-length λ both will remain inversely proportional to T .

If then we plot wave-length against radiation intensity, or λ against E_λ , we can pass from the curve for the temperature T of any body whose radiation is purely thermal to its corresponding curve at the temperature T' , by changing all the wave-lengths in the proportion of T to T' , and the value of the shifted E_λ in the proportion of T'^5 to T^5 .

The position of maximum radiation is the easiest to determine on a radiation curve. Calling this λ_m , we have the fact that E_{λ_m} varies directly as T^5 . This too furnishes a method for comparing the temperatures of full radiators.

COMPLETE RADIATION EQUATION

In the foregoing there is nothing to show what is the actual distribution of the energy in the spectrum of a black body at any given temperature. The equations only show how the total energy, the energy of any given region, and the wave-length are related to the absolute temperature.

Several attempts have been made to find an expression for the distribution of energy in the spectrum of a full radiator at any given temperature, but some of the assumptions and methods of treatment have been questioned, and no effort will be made to give their substance here.

From electromagnetic considerations Planck¹ obtained the following equation:

$$E_{\lambda} = C_1 \frac{\lambda^{-5}}{e^{\frac{C_2}{\lambda T}} - 1}$$

in which C_1 and C_2 are constants, T the absolute temperature, E_{λ} the intensity of the energy of the wave-length λ , or the ratio of q to $d\lambda$, where q is the energy between λ and $\lambda + d\lambda$, and e the Naperian base.

Larmor² has also derived this equation, and by a different method.

While the reasoning that led to this equation is not so obvious, and may not be so certainly correct as that that has given the Stewart-Kirchhoff, the Stefan-Boltzmann, and certain other radiation and absorption laws, it probably is the best general radiation equation that has been devised, and agrees almost exactly with the observations from 85° C. to 1773° C. by Rubens and Kurlbaum.³

¹ *Annalen der Physik*, **4**, 553, 1901.

² *Proc. R. S., A*, **83**, 81, 1909.

³ *Annalen der Physik*, **4**, 649, 1904.

RADIATION AND REFRACTIVE INDEX OF ADJACENT MEDIUM
KIRCHOFF-CLAUSIUS LAW

Let single wave-length radiation have its origin at O_2 , Fig. 1, where the refractive index for this radiation is μ_2 . Let this radiation, filling an infinitesimal solid angle, pass across the interface AB into a medium of smaller refractive index, μ_1 , and let the index-change be so gradual that there is no reflection.

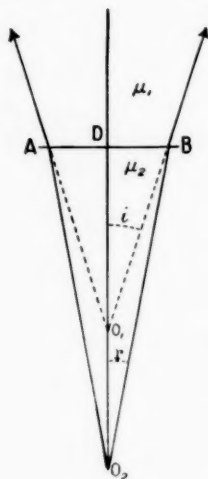


FIG. 1

The radiation that leaves O_2 will, to an observer in the outer medium, appear to come from O_1 , and therefore

$$\frac{O_2 D}{O_1 D} = \frac{\sin i}{\sin r} = \frac{\mu_2}{\mu_1}.$$

Let ω_1 and ω_2 be the corresponding small solid angles filled by the radiation at O_1 and O_2 respectively.

Then

$$\frac{\omega_2}{\omega_1} = \left(\frac{O_1 D}{O_2 D} \right)^2 = \left(\frac{\mu_1}{\mu_2} \right)^2.$$

Therefore, if R_1 and R_2 represent the flux of energy through unit solid angles from O_1 and O_2 respectively, then

$$\frac{R_1}{R_2} = \frac{\omega_2}{\omega_1} = \left(\frac{\mu_1}{\mu_2} \right)^2.$$

This, of course, holds for every direction from O_2 , or for the solid angle 4π .

The total radiation, therefore, from a given object varies directly as the square of the refractive index of the surrounding medium.

This law, presumably, applies equally to both luminescence and incandescence, and advantage might well be taken of it in certain delicate radiation experiments.

DISCONTINUOUS RADIATION

Solids and liquids, with but few exceptions, yield continuous, though not strictly black body, or full radiator spectra; while gases give radiations that differ so greatly in intensity from one wave-

length to another that, except when the gas layer has considerable depth or density, they may be regarded as absolutely discontinuous. Possibly the radiations given out by an isolated luminous particle are strictly discontinuous.

Each element yields its own discontinuous, or line, spectrum. Many of the elements, in addition to, so far as known, wholly unrelated lines, give series of lines whose wave frequencies are very approximately connected together by simple mathematical relations; though the reason for this, the underlying physical cause, is not known. Most of the elements, however, yield only a bewildering multitude of lines that have no known orderly, or series, relation to each other.

The method of rendering the gases luminous, whether by mere heating, by electric arc or spark, or otherwise, has great influence on their resulting spectra; but chiefly, if not entirely, on the number, and on the absolute and relative intensities of the lines.

INFLUENCE OF MAGNETIC FIELD ON SPECTRAL LINES ZEEMAN EFFECT

When the strength of the magnetic field in which a luminous gas is situated is changed, its spectrum is correspondingly modified. Many lines are changed in a complex and most puzzling manner, but whatever modification applies to one line of any given series applies equally to all the other lines of the same series; but not, in general, to the non-series lines nor to the lines of some other series.

In the simplest cases a single non-polarized line becomes a polarized triplet, when viewed across the lines of force. The middle component retains the same wave-length as the original line while the others are displaced equally, or nearly so, to either side. All three components are plane polarized, the middle line being polarized in one plane, and the side lines in a plane at right angles to this. When viewed along the lines of force two oppositely circularly polarized spectral lines are seen, displaced equally to either side of the original.

Inasmuch as the luminous particle is acted upon by a magnetic field, as this Zeeman phenomenon shows, it is clear that, for the time being at least, it must possess a magnetic field of its own, due, conceivably, to orbital rotations of electrons.

If the frequency of the vibration is a direct function of the orbital rotation of the electron, and this seems probable, then the magnetic field of the particle, due to the rotating electron, must also be proportional to the frequency, or inversely proportional to the wavelength. But changing the magnetic field within the orbit of such a rotating electron will simply alter proportionately its period of rotation.¹ Therefore, with N for the magnetic field due to the rotating electron, we can write

$$\frac{\delta\lambda}{\lambda} = \frac{\delta N}{N}.$$

But $\delta N = H$, the strength of the disturbing external magnetic field. Therefore, remembering that N is inversely proportional to λ , we get $\frac{\delta\lambda}{H\lambda^2} = \text{a constant}$. And this, regardless of whether the above conception even remotely agrees or not with the real structure and behavior of luminous particles, is the fundamental Zeeman equation, as established by experiment.

PRESSURE DISPLACEMENT

As a luminous particle is more and more crowded by the presence of other particles, their nature apparently making but little difference, the frequency of its vibrations is gradually decreased. The experimental evidence, extending over a pressure range of 200 atmospheres, indicates that for any line we can write, at least approximately,

$$\delta\lambda = K(p_2 - p_1); p_2 > p_1,$$

in which K is a constant, different however for different lines, and p the pressure. For any given group of lines, $\delta\lambda$ increases with λ , but for the non-series lines the irregularities in this particular are very great, though, in general, the same law holds for them also.

When confined to the *same* Mendeléjeff group of elements, $\delta\lambda$, in the case of *analogous* lines, increases with atomic weight.

EMISSION AND ABSORPTION OF RADIATION BY GASES

When a high-temperature flame, such as that of a Bunsen burner, contains the vapor of a metal or some compound of it, it generally

¹ Langevin, *Journal de Physik* (4) 4, 678, 1905.

gives out radiations characteristic of this metal. And when radiations of these particular frequencies are incident upon the flame they are absorbed to a greater or less extent. Such radiations, however, as the hot gas does not emit it does not absorb. Let a layer of gas of constant composition and density, and of unit thickness, emit normally to its bounding planes a given radiation of intensity R_1 , and let it so absorb radiation of this same wave-length that only the n th part of that incident normally on one side gets through at the other. Then its coefficient of absorption in this case, the fraction of the incident given radiation absorbed by a layer of the gas of unit thickness, is $1 - \frac{1}{n}$, or $\frac{n-1}{n}$, a value independent, apparently, of intensity. The maximum intensity, therefore, of this radiation that this gas could give would be from a layer of infinite thickness, and is expressible as

$$R_{\infty} = R_1 + \frac{R_1}{n} + \frac{R_1}{n^2} + \text{etc.} = \frac{nR_1}{n-1}.$$

In other words, the maximum radiation intensity for a mass of gas, however deep, is given by the radiation intensity of a layer of any thickness whatever divided by the coefficient of absorption of that same layer.

When the spectrum of an incandescent solid is taken through a colored flame the appearance will depend upon the relative brilliancy at that place of the solid to the flame. Let the depth of the flame be such as to give R_{∞} , then, calling S the intensity of the radiation of the solid over a narrow spectral region, we have,

where $S > \frac{nR_1}{n-1}$, a dark line on a bright background;

where $S = \frac{nR_1}{n-1}$, uniform brilliancy—no line visible; and

where $S < \frac{nR_1}{n-1}$, a bright line on a relatively dark background.

The first case gives the phenomenon of true reversal, so conspicuously seen in the solar spectrum.

In the case of many metallic lines, of certain hydrogen lines, of the bands of cyanogen, and of the bands due to the fluorides of cal-

cium, barium, and strontium, there often occurs what is known as spontaneous reversal. Here the cooler vapors surrounding the flame absorb greatly the radiations from the hotter vapors nearer its center, radiations which the cooler vapors themselves would send out at higher temperatures, and thereby produce lines with bright centers and dark sides.

TRANSMISSION OF SINGLE WAVE-LENGTH RADIATION LAW OF BOUGUER

When an observer is on that side of an absorbing medium away from the source of radiation, it is easy for him, by varying the thickness of the absorbing layer, to determine the coefficient of transmission for a given wave-length and intensity of the incident radiation, provided that there is no disturbance due to internal reflections.

Let the absorbing medium be a uniform one and let the intensity of the incident radiation be I_o . Let a be the fraction of the incident radiation transmitted a unit distance, then for distances m and n we obtain, respectively, $I_m = I_o a^m$, and $I_n = I_o a^n$ (equation of Bouguer) in which I_o and a are unknown, but the other terms known. By combining the two equations we get

$$a = \left(\frac{I_m}{I_n} \right)^{\frac{1}{m-n}}, \text{ and } I_o = I_m \left(\frac{I_m}{I_n} \right)^{\frac{m}{n-m}}.$$

For convenience of computation, if practical, let $n = 2m$. Then

$$a_m = \frac{I_n}{I_m},$$

and

$$I_o = \frac{I_m^2}{I_n}.$$

These equations are used in determining the transmissibility of the atmosphere to various solar radiations, and to finding their intensities just outside the absorbing medium.

TRANSMISSION OF MULTIPLE WAVE-LENGTH RADIATION LANGLEY'S LAW

It might seem at first that the above absorption equation for single wave-length radiation would apply to radiation of any complexity whatsoever. But, as Langley has shown, it does not.

Let the intensities of the incident single wave-length radiations be A_o, B_o, C_o , etc., and their respective coefficients of transmission a, b, c , etc. Then their combined intensity, through the thicknesses m and $2m$, will be

$$A_o a^m + B_o b^m + C_o c^m + \text{etc.} = R_m,$$

and

$$A_o a^{2m} + B_o b^{2m} + C_o c^{2m} + \text{etc.} = R_{2m},$$

respectively.

The intensity of the incident radiation, according to the Bouguer formula, is

$$R_o = \frac{R_m^2}{R_{2m}}.$$

The difference between the real and this calculated value of the intensity of the incident radiation is

$$\begin{aligned} A_o + B_o + C_o + \text{etc.} - R_o &= A_o + B_o + C_o + \text{etc.} - \frac{(A_o a^m + B_o b^m + C_o c^m + \text{etc.})^2}{A_o a^{2m} + B_o b^{2m} + C_o c^{2m} + \text{etc.}} = \\ &= \frac{A_o B_o (a^m - b^m)^2 + A_o C_o (a^m - c^m)^2 + \dots + B_o C_o (b^m - c^m)^2 + \text{etc.}}{A_o a^{2m} + B_o b^{2m} + C_o c^{2m} + \text{etc.}}. \end{aligned}$$

An occasional term in the numerator may reduce to zero, since possibly $a=k, c=l$, etc., but, in general, no two of the coefficients a, b, c , etc., are equal to each other. Therefore every term, except the few zero ones, if such exist, and consequently the whole fraction, is real and positive, and the value of the intensity of the radiation, calculated according to the Bouguer formula, too small. The error in using this equation consists in the assumption that the coefficients of transmission are the same for radiations of all wave-lengths.

Integrating pyrheliometers, therefore, give values of the solar constant that are too small.

THE ÅNGSTRÖM PRESSURE EFFECT

Ångström¹ has shown that the absorption of radiant energy by carbon dioxide increases with the density as well as with the quantity of the absorbing gas; and also² that the effect is the same, both qualitatively and quantitatively, whether the given increase in pressure be secured by compression into a shorter column of the pure carbon dioxide or by the addition of an inert gas.

¹ *Annalen der Physik*, **6**, 163, 1901.

² *Arkiv för Matematik, Astronomi och Fysik*, **4**, No. 30, 1908.

A column of carbon dioxide ten centimeters long gave a certain absorption, but when it was expanded into a column of thirty centimeters length, the cross-section and the temperature remaining the same, the absorption was found to be decidedly less. However, on pumping an inert gas into this new volume until a pressure was obtained equal to the original pressure in the ten-centimeter column the absorption was increased up to its first value.

This interesting investigation recently has been extended¹ to carbon monoxide, water vapor, and a number of other gases, all of which show the same phenomenon, but to unequal extents. In all cases so far examined it is most pronounced at pressures below one atmosphere.

This property of gases introduces complications into the absorption of radiation as it passes through atmospheres of varying density, such as that surrounding the earth.

SUMMARY

The following are the principal laws of radiation and absorption.

1. *Prevost's theory of exchanges*.—In the case of full radiators we have

$$G = KC(T_1^4 - T_2^4),$$

in which G is the energy gain per second by the black body at the absolute temperature T_2 from some other black body at the absolute temperature T_1 , C the absolute emissive power of a unit area of a black surface, or its total radiation per unit time when at the absolute temperature 1°C ., and K a constant depending upon the distance between the two objects and their sizes. If this distance is r centimeters, and their cross-sections at right angles to r , A and A' square centimeters respectively, then

$$K = \frac{AA'}{r^2}.$$

Also, with one square centimeter for the unit area,

$C = 5.32 \times 10^{-5}$ ergs per second, or 5.32×10^{-12} watts (Kurlbaum).

Therefore,

$$G = \frac{AA'}{r^2} 5.32 \times 10^{-5} (T_1^4 - T_2^4) \frac{\text{ergs}}{\text{second}}.$$

¹ E. v. Bahr, *Annalen der Physik*, **29**, 780, 1909.

2. *Lambert's cosine law*.—This is expressed by the equation

$$R_{\theta} = R_n \cos \theta,$$

in which R_n is the radiation per unit area normal to the full radiator, or black surface, and R_{θ} its corresponding radiation in a direction θ degrees from the normal.

3. *Stewart-Kirchhoff law*.—The most complete expression of this law is given by the equation

$$\left(\frac{E}{A} \right)_{\lambda, \phi, T} = (R)_{\lambda, \phi, T},$$

in which E is the radiation per unit area and time of any object, H the radiant energy incident during the same time upon this area, A the energy it absorbs, and R the corresponding radiation of an equal black body surface—all at the same temperature T , and restricted to the same state of polarization ϕ , and the same spectral region λ , which, however, may cover any range from single wave-length to full radiation.

4. *Energy of radiation*.—The energy per (centimeter)³, say, along a train of uniform radiation, is half kinetic and half potential, and the kinetic proportional to $\left(\frac{a}{\lambda} \right)^2$, in which a is the amplitude and λ the wave-length. If we restrict the consideration to a (centimeter)² and a single wave-length in depth we will find that the kinetic energy, still equal to the potential, is proportional to $\frac{a^2}{N\lambda^2}$, or to $\frac{a^2}{\lambda}$, in which N is the number of wave-lengths per centimeter.

5. *Light pressure—Maxwell-Bartoli effect*.—When the radiation is unidirectional and the receiver a black body, $p=e$, in which p is the pressure per unit surface at right angles to its direction and e the density of the radiation energy. If the receiver is a perfect mirror

$$p = 2e \frac{c \pm u}{c \mp u},$$

in which c is the velocity of light and u the velocity of the mirror with reference to the source; the upper signs being used when the mirror is moving toward the radiator. When $u=0$, $p=2e$.

If the radiation is perfectly diffused,

$$p = \frac{1}{3}E,$$

in the case of all non-diathermanous objects, in which E is the energy density of the diffused radiation.

6. *Stefan-Boltzmann law*.—This is generally expressed by the equation

$$R = CT^4,$$

in which R is the complete radiation, or total radiation in all directions, of a black body at the absolute temperature T , while the constant $C = 5.32 \times 10^{-5}$ ergs per second per square centimeter (Kurlbaum).

7. *Wien's displacement law*.—This law states that

$$\lambda T = \text{a constant},$$

in which λ is the wave-length corresponding to any given point on the radiation-energy curve, and T the absolute temperature. As a special and important case we can write $\lambda_m T = A$, in which λ_m is the wave-length of maximum intensity. If λ is expressed in thousandths of a millimeter or microns, then $A = 2940$, according to Lummer; or 2921, according to Paschen.

8. *Temperature effect on the spectrum*.—A simple expression for this effect is $\phi(\lambda)T^{-5} = \text{a constant}$, in which $\phi(\lambda)$ is the ordinate in a normal spectrum energy-curve, or a curve in which the abscissae are proportional to wave-lengths, and T , as usual, the absolute temperature. An important special case is $\phi(\lambda)_m T^{-5} = \text{a constant}$, in which $\phi(\lambda)_m$ is the ordinate corresponding to the wave-length, λ_m , of maximum intensity.

9. *General radiation equation*.—Presumably the best general equation is

$$E_\lambda = C_1 \frac{\lambda^{-5}}{e^{\lambda T} - 1},$$

due to Planck, in which E_λ is the ratio to $d\lambda$ of the energy belonging to the spectral region between λ and $\lambda + d\lambda$, e the Naperian base, $C_2 = 4.965$, $\lambda_m T = 14,500$ (Paschen); 14,600 (Lummer), and $C_1 = 3.073 \times 10^7$, on the assumption that $E_{\lambda_{max}} = 1000$ when $T = 1000^\circ \text{C}$.

10. *Radiation and refractive index—Kirchhoff-Clausius law.*—

$$\frac{R_1}{R_2} = \left(\frac{\mu_1}{\mu_2} \right)^2.$$

Here R_1 is the radiation per unit area and time of a black body in a medium whose refractive index is μ_1 , while R_2 is its corresponding radiation, when in a medium whose refractive index is μ_2 .

11. *The Zeeman effect.*—Radiation that ordinarily appears, when viewed in a spectroscope, as a single line, yields multiple polarized lines when the source is in a strong magnetic field.

The displacement of a component line from the original position, and its general dependence upon the strength of the magnetic field and the wave-length are shown in the equation

$$\frac{\delta\lambda}{H\lambda^2} = A.$$

Here $\delta\lambda$ is the displacement of the component, λ the original wave-length, H the strength of the magnetic field, and A a constant for any given line or series of lines, but different for different series.

12. *Pressure shift.*—When the pressure is increased about the source of radiation, the period of vibration is slightly increased, and the position of the line correspondingly shifted toward the region of longer wave-lengths. The amount of this for any given line is closely expressed by the relation

$$\delta\lambda = K(p_2 - p_1),$$

in which p is the pressure and K a constant that depends upon the line and the element to which it is due.

13. *Bouguer's law of absorption.*—This is expressed by

$$I_m = I_o a^m,$$

in which I_o is the intensity of the incident radiation, a the coefficient of transmission, or the ratio of the radiation that gets through a layer of unit thickness of the absorbing medium to the incident radiation, m the thickness traversed, and I_m the intensity after the radiation has passed through a layer of thickness m .

This law applies rigidly only for single wave-length radiation, and to media that are without internal reflection.

14. *Absorption as affected by pressure—Ångström effect.*—The coefficient of absorption of many gases (all that have been examined) increases with increase of pressure; and this increase, while different for different gases, and most pronounced when the pressures are below one atmosphere, is the same, in every particular, whether the given increase of pressure is due to compression of the absorbing gas or to the addition of an inert one.

15. *Type of absorption independent of temperature.*—So long as its physical phase and its chemical composition remain unchanged, a body continues to absorb the same wave-length radiation, independent of change of temperature. This is of universal application, so far as known, and not restricted to full radiators.

16. *Increase of radiation with increase of temperature.*—Every wave-length radiation that an object emits increases in intensity with increase of temperature, so long as its physical phase and chemical composition are unaltered. This, too, so far as we know, is of universal application.

LITERATURE

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In closing I wish to thank Professor Henry Crew for his kind criticism and various helpful suggestions.

MOUNT WEATHER OBSERVATORY, VA.

THE ABSORPTION SPECTRUM OF SULPHUR DIOXIDE

By FRANCES LOWATER

In some earlier work on sulphur dioxide¹ the author obtained an absorption spectrum, which exhibited marked changes with change of pressure and change in the length of the column of gas. The change in the absorption with the reduction in the absorbing medium consisted not merely in a reduction in the width of the region, but also in breaking up very wide absorption bands into narrow bands.

With a column of gas 207 cm in length and at a pressure of from one to three atmospheres the spectrum consisted of:

Narrow bands from λ 3900 to 3333
One wide band from λ 3330 to less than 2100

At a pressure of 1.5 cm of mercury it consisted of:

Narrow bands from λ 3226 to 3146
One wide band from λ 3134 to 2467
Narrow bands from λ 2456 to 2297
One wide band from λ 2290 to less than 2100

At a pressure of 0.13 cm it consisted of:

Narrow bands from λ 3180 to 2970
One wide band from λ 2968 to 2715
Narrow bands from λ 2702 to 2269
One wide band from λ 2250 to less than 2100

When the length of the column of gas was reduced to 20 cm and the pressure was less than 1 cm of mercury, the whole spectrum consisted of narrow bands lying within the region λ 3133 to 2200.

The changes in the spectrum produced by change of pressure suggested that with the gas at a suitable pressure and with spectral apparatus of greater dispersion the bands of the spectrum might be broken up into lines.

OBJECTS OF INVESTIGATION

The present investigation was undertaken to determine whether the bands of absorption could be broken into lines and, if so, whether

¹ *Astrophysical Journal*, 23, 324, 1906.

a relationship existed between the wave-numbers of lines of similar physical character.

In the case of sulphur dioxide a special value is attached to the absorption spectrum and its resolution into lines, as its emission spectrum is so difficult to obtain, on account of the great tendency of the gas to dissociate, even when a very weak discharge is passed through it. So far its emission spectrum¹ is known only as a band spectrum with heads toward the ultra-violet, and its investigation has not been carried into wave-lengths less than 3270; the author, however, intends to make a further attempt in this direction at the first opportunity. No resemblance between the emission and absorption spectrum has yet appeared. This fact is true also of chlorine, but in the case of iodine, Konen has found that the absorption spectrum corresponds with the band emission spectrum from a vacuum tube.

APPARATUS AND MANIPULATION

The source of light was the spark of an alloy of cadmium and zinc mixed in atomic proportions; this light gives a continuous spectrum down to λ 2100, provided a sufficiently long exposure is given and a suitable capacity is placed in parallel with the spark, across the terminals of the secondary of an induction coil.

The spectral apparatus was a concave Rowland grating, of 180 cm radius of curvature, with 15,028 lines to the inch (592 to the mm, approximately) and the width of the ruled surface 6.2 cm. The photographic plates used were Seed's No. 27 Gilt Edge on lantern-slide glass.

The gas was inclosed in steel tubes which had been thoroughly cleaned and their ends closed with quartz plates. At the beginning of the investigation, a tube 20 cm in length was used, but as the spectrum obtained was not well defined, a tube 80 cm long was adopted and better results were obtained.

The tube was exhausted by a Geissler pump and the pressures read by a McLeod gauge. The gas was obtained from liquid sulphur dioxide which had been redistilled, and care was taken that the gas used in the tube should be free from air; its high temperature of liquefaction (-10° C.) insures its freedom from other gases.

¹ *Astrophysical Journal*, 23, 338, 1906.

The beam of light from the spark was made parallel by a quartz lens before entering the tube; on emergence it was brought by a second quartz lens to a focus on the slit of the grating apparatus. For comparison a photograph of the spectrum of the unabsorbed light of a second spark of the same alloy was taken immediately above or below that of the absorption spectrum of the gas. The beam from this second spark was made parallel by a third quartz lens and when required was brought between the end of the absorption tube and the second quartz lens which focused the light on the slit.

For determination of the wave-lengths of all the lines, measurements of the photographic plates were made in the usual way by means of a dividing engine; on the one used for this purpose readings could be made to 0.0001 mm, that is, to a greater degree of accuracy than that to which settings could be made on the absorption lines. The reduction factor was roughly 9.3 Å to 1 mm.

STANDARD LINES

Metallic lines of cadmium, zinc, lead, and iron were transmitted through the gas, the lead and iron appearing from impurities in the two other metals. Certain cadmium lines were used as standards of reference; intermediate lines of cadmium, zinc, lead, and iron were used for plotting a curve of errors, which was applied in the usual manner for the correction of the calculated values of the unknown lines. By using as lines of reference those transmitted through the gas, one avoids possible errors due to displacement of standard lines by want of perfect adjustment of another source. A further advantage in having the reference lines superposed on the spectrum to be investigated is that the plate can be placed under the microscope of the dividing engine, so that lines stretch continuously across the whole field of view, and this makes easier the exact adjustment of the cross-hair parallel to the lines.

The best values known of the wave-lengths of cadmium and zinc in the region in which this spectrum lies, namely λ 2700 to λ 3200, were those determined by Eder and Valenta;¹ these were based on

¹ *Normal-Spectren einiger Elemente zur Wellenlängenbestimmung im äussersten Ultraviolett*, 1899.

their own values of iron lines which were referred to Rowland's normals.

The last photograph for the present work was taken before the publication of Fabry and Buisson's iron standards¹ reached this country, March 1908; otherwise a photograph of iron lines would have been taken on the same plate as the absorption spectrum and measurements on these lines compared with those made on the lines of reference transmitted through the gas. It was considered that Fabry and Buisson's standards would form a more uniform basis for a relationship among wave-numbers, hence the wave-lengths of the standard lines were referred to these normals by the following plan. A curve was plotted having as abscissae wave-lengths of iron lines and as ordinates the ratios of Rowland's wave-lengths to those of Fabry and Buisson's of the same lines. From this curve was read off the ratio by which Eder and Valenta's wave-lengths must be divided to give their values referred to Fabry and Buisson's normals. The wave-lengths of the lines used for this curve are given in Table I, together with the ratio of their values as determined by Rowland and by Fabry and Buisson.

TABLE I

Rowland's Value*	Fabry and Buisson's Value	Rowland's λ
		Fabry and Buisson's λ
2435.247	2435.159	1.00003601
2506.994	2506.904	3590
2528.599	2528.516	3322
2679.148	2679.065	3098
2778.340	2778.225	4135
2813.388	2813.290	3483
2851.904	2851.800	3646
2912.275	2912.157	4052
2987.410	2987.293	3916
3075.849	3075.725	4032
3225.907	3225.790	1.00003627

* *Philosophical Magazine* (5), 36, 49, 1893.

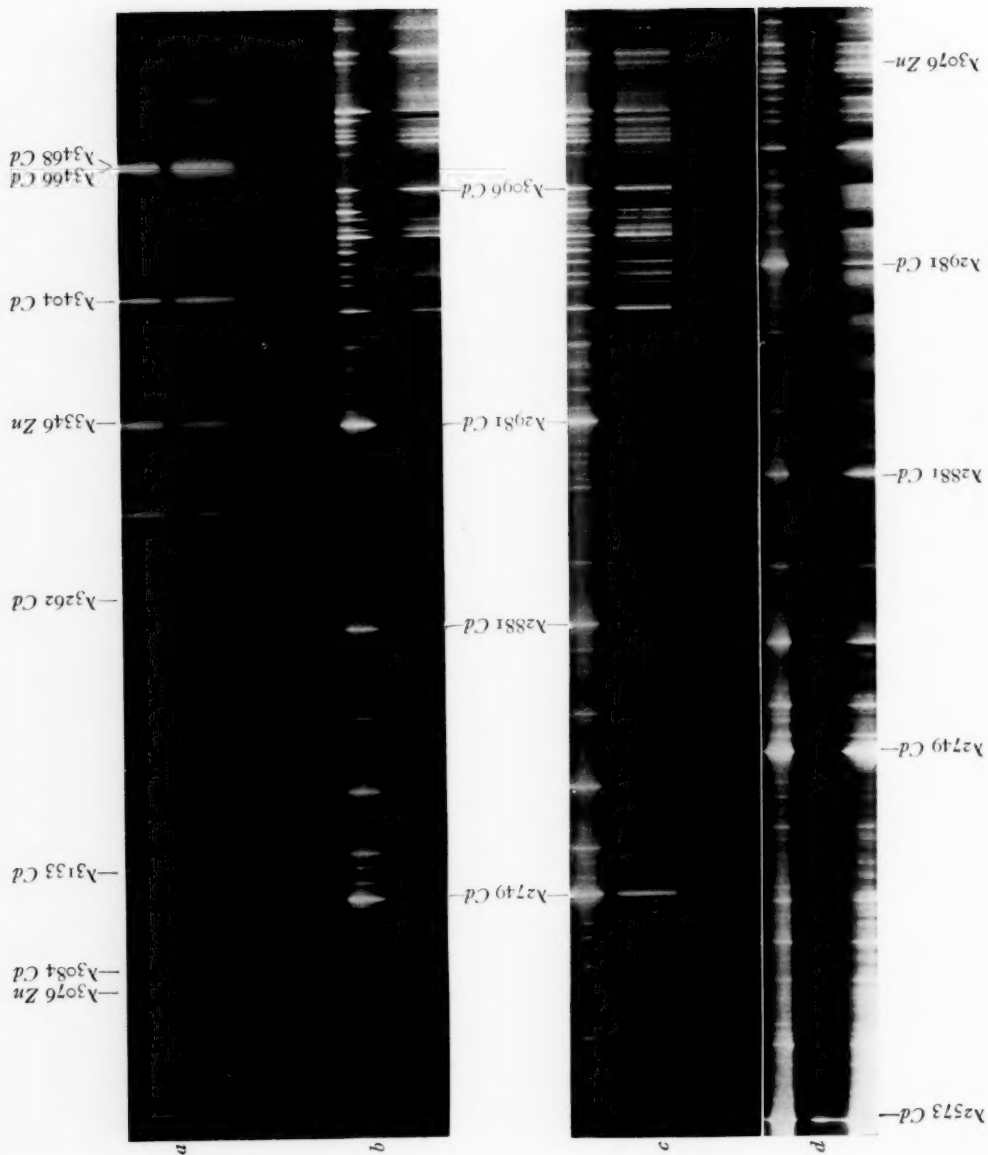
The cadmium standards used for the regions lying between them have the following wave-lengths when referred to Fabry and Buisson's normals:

2707.05	3080.877
2833.073	3133.228
2996.049	

¹ *Journal de Physique* (4), 7, 169-193, 1908.

1904

PLATE IX



ABSORPTION SPECTRUM OF SULPHUR DIOXIDE
(All the fine lines are lost in the engraving)

DETERMINATION OF EXPERIMENTAL CONDITIONS FOR BEST DEFINITION

Photographs of the spectrum were taken first with a column of gas 20 cm in length and with the gas under various pressures and the plates were given different times of exposure. These experiments showed that the bands obtained in the earlier work could be broken into lines, but so far the lines were not well defined. The experiments were repeated with a column of gas 80 cm in length until conditions were found which gave the best-defined lines. These conditions were a column of gas 80 cm long, a pressure of about 1 mm, and an exposure of four hours. With smaller pressure the absorption was too weak to give clear lines; with greater pressure the bands were not completely broken up into lines. Similar effects were produced with different exposures; with too long an exposure, too much was transmitted; with too short an exposure, not sufficient light was transmitted to give clear lines.

RESULTS

The spectrum under different pressures is shown on Plate IX. The positives from which the reproductions are made are threefold enlargements of the original negatives. Much of the detail of the negatives is lost even in the positives, but for reproduction, enlargement was necessary, as it requires a magnifying glass to show the lines on the negatives.

The spectrum is shown on Plate IX under the following conditions:

Fig.	Length of Column of Gas	Pressure of Gas
<i>a</i>	20 cm	1 atmos.
<i>b</i>	80	3 mm
<i>c</i>	20	5
<i>d</i>	80	0.8

The spectrum was found to consist of about 590 lines lying between λ 2707 and 3120; the absorption extended to shorter wave-lengths but the lines were much less clearly defined. The wave-lengths were determined as described above and expressed in Ångströms; the wave-numbers were then calculated as $\frac{1}{\lambda} \times 10^8$ and therefore represent the number of vibrations executed while the wave is propagated through one centimeter. The wave-lengths, λ , of the lines, with their intensities, *I*, are given in Table II, the intensities being estimated by eye from 10, the greatest, to 1, the least.

TABLE II

A	I	A	I	A	I	A	I
2707.6	7	2780.85	7	2807.18	7	2820.70	8
10.28	6	81.43	8	07.56	7	30.38	9
22.33	8	81.96	6	08.03	6	30.85	10
25.84	7	82.50	6	08.41	6	31.38	10
26.22	7	82.98	6	09.30	6	31.83	10
26.73	7	83.47	7	09.66	6	32.24	10
28.04	5	84.01	7	10.07	7	32.78	10
28.56	5	84.52	7	10.3	7	33.47	9
29.03	5	84.93	7	10.73	8	33.86	9
33.42	8	85.22	7	11.03	7	34.27	9
35.66	7	86.38	6	11.51	8	34.79	9
36.61	7	86.60	6	11.88	7	35.15	9
37.48	6	87.02	6	12.28	8	35.58	8
37.86	6	87.30	6	12.70	7	35.91	8
38.61	6	87.72	8	13.20	7	36.23	8
39.2	8	88.24	8	13.60	7	37.46	8
39.92	6	88.66	8	14.21	8	37.85	8
40.46	6	88.96	9	14.57	8	38.19	8
40.8	6	89.50	9	14.85	8	38.63	8
41.18	6	90.06	9	15.35	9	39.02	7
41.65	5	90.58	8	15.80	9	39.33	7
42.0	6	91.06	8	16.1	9	39.79	6
42.3	5	91.49	7	16.5	9	40.29	7
42.84	5	91.82	7	16.93	9	40.55	7
52.94	2	92.14	7	17.22	9	41.00	7
53.43	3	92.68	7	17.59	9	41.61	7
53.91	3	93.07	7	17.99	10	42.06	7
54.4	4	93.37	7	18.46	10	42.46	7
55.02	4	93.86	6	18.71	10	43.15	8
59.12	5	94.32	6	18.97	10	43.60	8
60.02	5	94.74	6	19.26	9	43.99	8
60.60	5	95.13	6	19.65	9	44.40	8
61.32	5	95.58	6	20.13	9	44.74	8
61.97	5	95.93	7	20.48	9	45.27	7
62.80	5	96.65	8	20.79	9	45.60	7
63.39	5	97.13	9	21.12	9	45.91	7
64.29	5	97.62	9	21.53	9	46.31	7
64.75	6	98.08	8	21.78	9	46.81	8
65.24	7	98.91	7	23.42	6	47.27	8
65.75	6	99.31	7	23.76	6	47.68	9
66.16	4	99.70	6	24.16	7	48.16	9
66.52	4	2800.35	5	24.44	7	48.56	8
67.37	3	01.56	5	24.75	7	48.96	8
67.77	3	02.10	5	25.21	7	49.54	8
69.08	4	02.4	5	25.57	7	49.98	8
76.8	5	03.22	5	26.01	7	50.3	8
77.26	8	03.79	5	26.23	8	50.67	9
77.73	7	04.19	5	26.60	7	51.08	9
78.25	7	04.76	6	26.96	6	51.45	9
78.91	7	05.20	6	27.37	6	51.79	10
79.34	7	05.49	6	27.96	6	52.14	10
79.85	7	06.04	6	28.40	6	52.57	10
80.26	7	06.45	6	28.84	6	52.98	9
80.6	8	06.80	7	29.30	7	53.58	9

TABLE II—Continued

λ	I	λ	I	λ	I	λ	I
2853.92	9	2886.51	8	2920.2	8	2949.28	5
54.31	9	86.82	9	20.55	8	49.6	5
54.85	9	87.22	9	20.89	8	49.90	5
55.28	9	87.74	10	21.16	9	50.28	5
55.60	9	88.10	10	21.45	9	54.3	3
56.10	8	88.65	10	21.71	9	54.7	3
56.63	8	89.13	9	22.21	9	55.62	3
57.04	8	89.66	9	22.89	8	56.16	4
57.94	8	89.91	9	23.38	9	56.80	5
58.32	8	89.42	9	23.75	9	57.50	7
58.60	8	91.08	8	24.34	9	57.89	7
59.13	8	92.21	7	24.65	9	58.22	8
59.63	7	92.7	6	25.52	9	58.57	8
60.03	7	93.03	6	26.20	8	58.99	8
60.47	7	93.43	5	26.59	8	59.30	9
60.98	7	94.06	6	26.81	8	59.84	9
61.35	7	94.38	7	27.84	8	60.22	10
61.88	7	94.69	7	28.43	7	60.78	10
62.46	6	96.55	7	28.89	7	61.18	10
63.42	6	98.48	6	29.21	7	61.45	10
64.02	5	2900.27	9	29.56	6	61.98	10
64.9	7	01.15	9	30.01	6	62.40	10
65.64	8	01.56	8	30.33	6	62.83	9
65.98	9	01.96	8	30.69	5	63.27	9
66.5	10	02.62	8	31.10	5	63.72	9
66.82	10	03.30	8	31.72	5	64.82	8
67.38	10	04.37	8	32.95	4	66.04	8
67.87	10	04.8	7	33.50	4	67.40	5
68.62	9	05.20	8	34.69	3	68.05	5
68.97	9	05.81	8	35.11	4	68.34	5
69.21	9	06.14	8	35.52	4	69.09	5
69.66	9	06.49	10	36.38	5	69.76	5
70.31	9	07.17	10	37.2	5	70.51	3
70.76	9	07.90	10	38.07	10	71.70	1
71.32	9	08.2	9	38.5	10	72.91	1
72.19	8	08.6	9	39.10	9	73.57	1
72.72	8	08.98	8	39.63	10	74.33	1
73.1	8	09.86	8	40.06	9	74.8	1
73.72	8	10.13	8	40.41	9	75.89	1
74.1	8	12.04	5	40.79	9	78.2	8
74.43	8	12.36	5	41.18	9	78.55	8
74.95	8	13.28	5	41.57	9	79.13	9
75.55	8	13.55	5	41.97	9	79.85	8
76.92	6	14.3	4	42.83	9	81.66	5
77.62	5	15.25	4	43.40	9	81.99	5
78.01	6	16.1	5	43.93	9	83.40	6
78.35	7	16.53	6	44.39	9	84.79	6
79.86	5	16.82	7	44.82	9	86.13	5
82.73	3	17.42	8	45.64	9	88.02	4
83.5	3	17.74	8	46.09	9	88.77	4
83.79	4	18.31	9	46.65	8	89.46	3
84.4	4	18.94	8	47.23	8	90.27	2
85.1	5	19.35	7	48.55	6	93.8	2
85.93	8	19.66	7	49.00	5	98.0	5

TABLE II—Continued

λ	I	λ	I	λ	I	λ	I
2998.33	7	3021.18	10	3048.22	6	3083.21	5
99.0	9	21.62	9	49.46	6	84.02	6
99.56	9	22.15	9	49.82	5	85.63	7
99.81	10	22.68	9	50.46	4	86.20	7
3000.41	10	23.25	9	50.9	4	86.54	6
00.94	10	23.87	8	51.54	4	86.88	6
01.22	10	24.29	8	51.79	4	87.4	6
02.00	10	24.83	8	52.43	4	87.99	5
02.37	9	25.40	8	53.7	3	89.49	5
02.93	9	25.65	7	54.03	2	89.79	4
03.53	9	26.10	7	54.76	2	90.30	3
04.15	9	26.51	7	55.31	2	90.62	3
04.50	8	26.87	7	55.7	2	91.24	3
05.43	7	27.15	6	56.0	2	99.27	1
05.8	7	27.64	6	56.62	2	3101.2	3
06.2	5	28.10	6	57.15	2	03.0	1
06.55	4	28.72	6	57.73	2	04.16	1
06.96	4	29.25	5	58.38	2	05.29	2
07.40	4	29.87	5	61.72	7	05.81	2
07.99	3	30.4	5	62.48	8	06.36	5
08.58	3	33.8	3	63.11	8	06.89	5
09.35	3	34.7	3	63.7	8	07.43	4
09.87	3	35.2	3	64.10	7	08.08	2
10.33	2	37.1	2	64.4	8	08.66	1
10.87	2	37.6	2	65.46	8	09.26	1
11.42	2	38.0	2	65.71	7	09.86	3
12.29	2	38.5	2	66.49	7	10.73	3
13.00	2	39.5	3	67.0	6	11.18	1
13.56	2	40.07	4	67.76	6	11.77	1
13.88	2	40.8	3	70.02	2	12.27	2
14.82	1	41.43	10	70.57	4	13.61	2
15.28	1	41.79	10	71.20	4	14.18	2
15.86	1	42.03	10	75.31	3	16.1	2
16.59	2	42.40	9	78.3	3	16.9	1
18.1	2	43.14	9	79.0	3	17.3	1
18.83	8	44.0	8	79.74	3	17.8	1
19.26	8	44.96	8	80.31	3	18.2	1
19.63	9	46.00	8	81.5	3		
19.98	10	47.20	6	82.03	4		

STRUCTURE OF THE SPECTRUM

A curve was plotted having wave-numbers as abscissae and intensities as ordinates (see Fig. 1). The regularity of this curve suggested a relationship between the wave-numbers of lines of relatively equal intensity. With this clue as a guide, it was found that 92 per cent of the lines could be arranged in groups or series of lines, in each of which the *first* differences of consecutive wave-numbers were approximately constant, or that each series of wave-numbers formed an

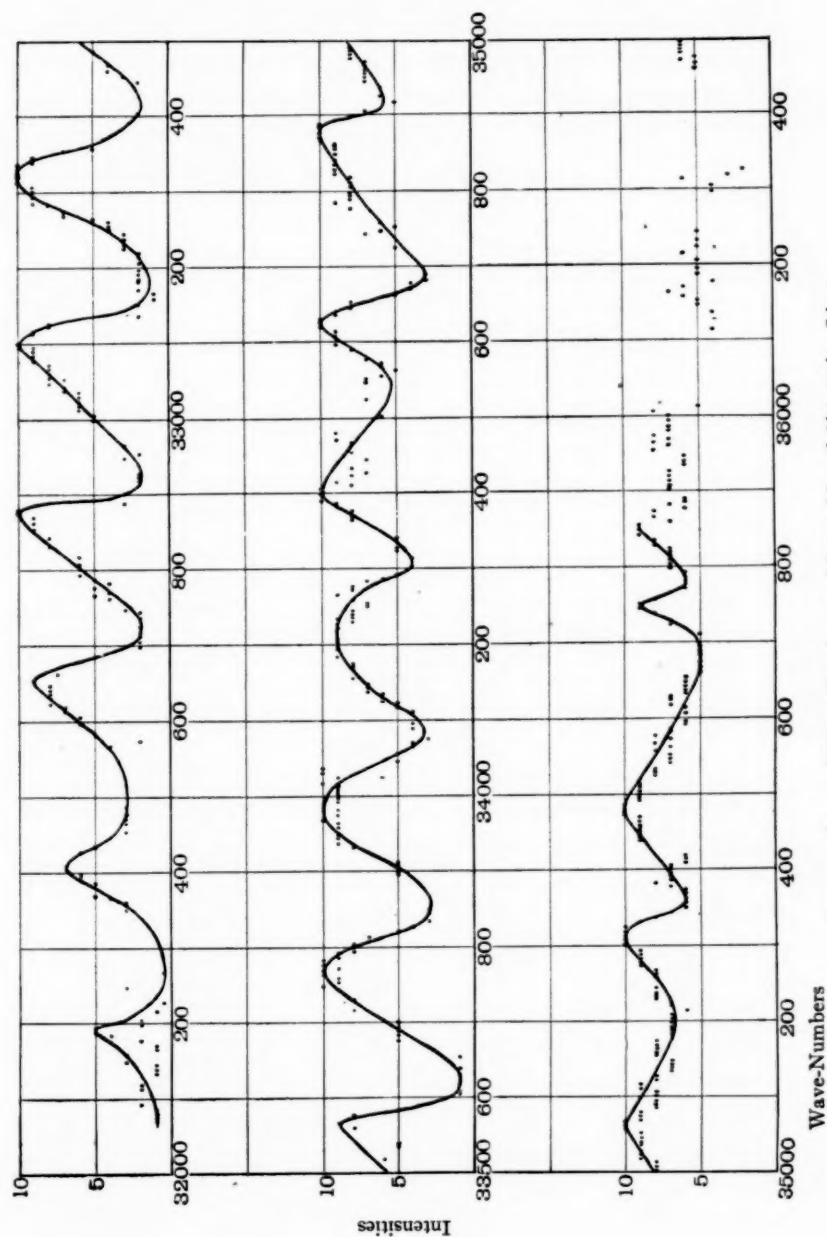


Fig. 1.—Curve of Wave-Numbers and Intensities of Absorption Lines

arithmetical progression; further, it was found that all these progressions, 44 in number, had approximately the same common difference, namely, 223. This equality of first differences is expressed by the simple equation:

$$N = a + bm \quad (1)$$

where

N = wave-number

a = constant

b = the common difference

m = the number of the term in its series,

= 1, 2, 3

It is to be noted that the spectrum of sulphur dioxide does not obey Deslandres' laws of equal *second* differences, between the lines of a band or between the heads of bands—laws which, as is well known, are expressed by a quadratic equation of the form

$$N = a + bm + cm^2,$$

where the first differences form arithmetical progressions. In the spectrum of sulphur dioxide the first differences are constant and the wave-numbers themselves form arithmetical progressions. Of the 586 lines in the region measured, only 47 do not appear in these 44 series; five of these 47 lines form a short series with the same mean common difference as the others; it is between series 43 and 44. In each series the greatest deviation of the common differences from their mean value is less than 1 per cent.

The 44 series of wave-numbers, with their first differences and intensities, are given in Table III; for convenience in reference, the wave-length of the line at the head of each column is inclosed in brackets above the column of differences. The wave-numbers which do not appear in this table are collected in Table IV, the five which form a short series being in the first column. In these tables N denotes the wave-number, D the first difference in wave-numbers, m the number of the term in the series, and I the intensity. Of the series found, that of lowest wave-numbers has been called the first; similarly for the terms in the series. Whether this series is really the first has not been determined; Plate IX shows that the spectrum extends into longer wave-lengths when the gas is at higher pressures,

but at these pressures measurable lines have not been obtained; hence it is undetermined whether or not the series extend into the region of longer wave-length. Thus the constant, a , in equation (1) has not been found. Apparently each series should have 23 terms, but none of the series is complete.

TABLE III

<i>m</i>	SERIES 44			SERIES 43			SERIES 42		
	I	N	D	I	N	D	I	N	D
23									
22									
21				7	36680.8	(2726.22) 222.2			
20	5	36466	(2742.3) 223	5	36458.6				
19	5	36243.4					5	36231.6	(2760.02) 224.9
18		2 × 225.3			3 × 223.9		8	36006.7	225.2
17	6	35792.8		6	35786.9		6	35781.5	223.2
16	8	35568.1	224.7	7	35563.3	223.6	8	35558.3	223.2
15	7	35344.4	223.7	8	35338.3	225.0			2 × 224.0
14	8	35121.4	223.0	9	35116	222	9	35110.4	224
13	8	34896.2	225.2	9	34892.1	224	10	34886.	225
12		2 × 222.3		4	34669	223	5	34661	225
11	8	34451.6		7	34443.6	225		2 × 224	
10	8	34229.6	222.0	9	34220.7	222.9	9	34212.7	221.9
9	9	34004.5	225.1	9	33995.5	225.2	9	33990.8	223.6
8	10	33781.3	223.2	9	33770.3	225.2	10	33767.2	223.8
7	8	33558.7	222.6		2 × 223.7				
6	10	33335.4	223.3	10	33322.9	223.3	10	33319.7	224.9
5				10	33099.6	224.2	9	33094.8	222.0
4		3 × 224.7		10	32875.4	222.1	10	32872.8	222.6
3	7	32661.4		9	32653.3			2 × 223.6	
2		2 × 223.3					6	32425.3	222.2
1	1	32214.8					2	32203.1	
	Mean differences 223.7			223.8			223.8		

TABLE III—Continued

m	SERIES 41			i	SERIES 40			i	SERIES 39		
	I	N	D		I	N	D		I	N	D
23 22	6	36896.6	(2710.28) 222.6								
21 20 19	7 5	36674.0 36222.8	2 × 225.6 222.2						6	36214.6	(2761.32)
18	7	36000.6	224.1	7	35993.9	(2778.25) 223.1					2 × 224.2
17	6	35776.5	223.5	6	35770.8	224.1		7	35766.3	224.6	
16	7	35553.0	221.9	7	35546.7	221.6		7	35541.7	223.2	
15	9	35331.1	225.6	10	35325.1	224.6		10	35318.5	225.1	
14	8	35105.5	223.6	8	35100.5	225.5		8	35093.4	224.3	
13	10	34881.9		10	34875.0	224.1		10	34869.1	225.2	
12		2 × 225.5		8	34650.9	225		8	34643.9	222.9	
11	8	34430.9	223.9	7	34426	223		8	34421.0		
10	9	34207.0		9	34202.6	221.7					
9		2 × 222.9		9	33980.9	224.5					
8	10	33761.2	222.8	9	33756.4	221.7					
7	5	33538.4		5	33534.7	223.6				9 × 223.6	
6		3 × 223.2		10	33311.1	222.0					
5				9	33089.1	2 × 224.6					
4	9	32868.8	222.3	8	32640	2 × 224					
3	8	32646.5	2 × 224.4					7	32408.3		
2				5	32192.0						
1	2	32197.7									
	Mean differences 223.7				223.6				223.9		
m	SERIES 38			i	SERIES 37			i	SERIES 36		
	I	N	D		I	N	D		I	N	D
23 22 21 20 19											
18	7	35979.8	(2779.34) 222.7						5	36194.8	(2768.80) 221.6
									8	35973.2	222.3

TABLE III—Continued

m	SERIES 38			SERIES 37			SERIES 36		
	I	N	D	I	N	D	I	N	D
17	8	35757.1	223.1				9	35750.9	225.0
16	8	35534.0	221.3	8	35529.4 (2814.57)	221.7	8	35525.9	224.9
15	10	35312.7	224.9	10	35307.7	224	10	35301.0	221.5
14	8	35088.0		8	35084	224.0	9	35079.5	223.8
13		2X223.9		9	34860.0	224.6	9	34855.7	2X222.9
12	9	34640.2		9	34635.4	221.6			
11		2X222.2		9	34413.8	221.7	8	34409.9	2X223.5
10	9	34195.7	221.4	9	34192.1	223.9			
9	9	33974.3	222.8	10	33968.2	221.7	9	33962.9	221.5
8	9	33751.5		10	33746.5		9	33741.4	222.6
7		2X222.3			2X222.8		6	33518.8	224.6
6	9	33307.0	223.8	9	33300.8	223.8	9	33294.2	223.9
5	9	33083.2	222.4	9	33077.0	225	8	33070.3	2X224.4
4	9	32860.8	224.8	9	32852				
3	8	32636.0			2X225		8	32621.5	222.7
2		2X224.8		7	32402.3	221.4	6	32398.8	224.6
1	5	32186.5		4	32180.9		2	32174.2	
	Mean differences 223.1			223.2			223.4		
	SERIES 35			SERIES 34			SERIES 33		
	I	N	D	I	N	D	I	N	D
23									
22									
21									
20									
19				5	36187.4 (2763.39)	223			
18	7	35967.9 (2780.26)	223.2	8	35964	225	7	35960.2 (2780.85)	
17	9	35744.7	225.1	8	35738.8	224.9		2X225	
16	9	35519.6		9	35513.9	221.5	9	35510	222
15		2X222.6		9	35292.4	222.5	9	35287.6	221.9

TABLE III—Continued

	SERIES 35			SERIES 34			SERIES 33		
<i>m</i>	I	N	D	I	N	D	I	N	D
14	9	35074.4		9	35069.9		10	35065.7	
			221.6			222.6			
13	9	34852.8		9	34847.3				
			223.6			222.5			
12	10	34629.2		10	34624.8				3×222.7
			224.6						
11	10	34404.6					10	34397.7	
			222.6						223.7
10	9	34182.0					8	34174.0	
			224.1						2×222.6
9	9	33957.9					8	33728.9	
									2×222.8
8			3×223.5			10×223.4	8	33283.4	
7									223.7
6	9	33287.4					8	33059.7	
			221.8						2×224.6
5	8	33065.6							
			224.4						
4	8	32841.2							
			222.3						
3	7	32618.9					7	32610.6	
			223.7						
2	6	32395.2		6	32390				
						222			
1				1	32168.2				
	Mean differences 223.3			223.3			223.3		

	SERIES 32			SERIES 31			SERIES 30		
<i>m</i>	I	N	D	I	N	D	I	N	D
23									
22									
21									
20									
19	4	36175.7	(2764.29) 223.0	6	36169.6	(2764.75) 223.7			
			224.6			222.8			
18	8	35952.7		6	35945.9				
			223			223.5			
17	7	35728.1		7	35723.1		6	35718.1	(2799.70) 222.1
			222						
16	9	35505		9	35499.6		9	35496.0	223.9
			221.1			2×221.8			
15	9	35282.5					9	35272.1	221.0
			222.0			222.1			
14	10	35061.4		10	35056.1		9	35051.1	223.9
			221.2			221.5			
13	9	34839.4		9	34834.0		9	34827.2	224.0
						223.4			
12	10	34618.2		9	34612.5		9	34603.2	222
			2×224.4			222.1			
11				10	34389.1		9	34381	
10	8	34169.5		8	34166.9				2×222
			221.0			223.6			

TABLE III—Continued

m	SERIES 32			SERIES 31			SERIES 30		
	I	N	D	I	N	D	I	N	D
9	9	33948.5		9	33943.3		9	33936.8	
8			2×222.6				8	33715.0	221.8
7	6	33503.2				3×223.4			2×223
6			2×224.8	7	33273.1		7	33269	
5	8	33053.5		7	33050.8	222.3	8	33045.8	223
4	8	32830.0	223.5						2×224.4
3	6	32605	225			4×223.8	6	32597.1	
2	5	32383.6	221						
1	1	32162.0	221.6	3	32155.8				
	Mean differences 223.0			223.0			222.9		
m	SERIES 29			SERIES 28			SERIES 27		
	I	N	D	I	N	D	I	N	D
23									
22									
21									
20									
19	7	36163.2	(2765.24) 224.3	6	36156.6	(2765.75) 223.9	5	36151.2	(2766.16) 224.8
18	6	35938.9		6	35932.7	222.9	7	35926.4	
17			2×223.8	5	35709.8	223.6			2×223.0
16	9	35491.3	225.1	10	35486.2	224.1	10	35480.4	222.3
15	8	35266.2	222.5	8	35262.1	222.6	8	35258.1	223.4
14	9	35043.7	222.5	9	35039.5	222.9	9	35034.7	224.5
13	9	34821.2		8	34816.6		8	34810.2	221.0
12			2×222.5				8	34589.2	223.3
11	8	34376.3	221.4			3×222.9	8	34365.9	223.3
10	8	34154.9		7	34148.0	2×224.2	7	34142.6	
9			3×222.2	5	33699.5	2×221.7			4×222.8
8	5	33488.2	223						
7	5	33265	224	4	33256.1	221.7	4	33251.3	222.3
6	7	33041.4	224.4	6	33034.4		6	33029.0	222.9

TABLE III—Continued

m	SERIES 29			SERIES 28			SERIES 27		
	I	N	D	I	N	D	I	N	D
4	6	32817.0					6	32806.1	
3			2X224.6			3X223.2			2X223.4
2	5	32367.8		4	32364.7		3	32359.2	
			221.7			222.6			223.1
1	3	32146.1		1	32142.1		1	32136.1	
	Mean differences 223.2			223.0			223.1		
	SERIES 26			SERIES 25			SERIES 24		
	I	N	D	I	N	D	I	N	D
23									
22									
21							8	36584.2	(2733.42)
20									2X224.4
19	5	36146.5	(2766.52)				4	36135.4	
									222.6
18				7	35919.4	(2784.01)	7	35912.8	
						225.0			225.3
17			3X223.1	5	35694.4		5	35687.5	
						224.1			222.1
16	10	35477.2		9	35470.3		9	35465.4	
									222.6
15			2X224.6			2X223.8	8	35242.8	
									223.9
14	9	35028.1		9	35022.8		9	35018.9	
			223			224.7			225
13	8	34805		8	34798.1		8	34794	
						222.5			224
12			2X221	7	34575.6		6	34570	
11	8	34362.7				2X223.0			2X222
			223.8						
10	7	34138.9		6	34129.6		6	34125.9	
			223.9			223.0			223
9	6	33915.0		5	33906.6		5	33903	
			223.0						223
8	5	33692.0					5	33680.4	
			225.0						221.8
7	4	33467.0				3X222.8	4	33458.6	
			222.2						2X223.6
6	3	33244.8		3	33238.3				
			221.8			221.2			
5	6	33023.0		6	33017.1		6	33011.5	
						224.4			222.7
4				6	32792.7		5	32788.8	
									221.6
3			3X222.3			2X221.6	4	32567.2	
2	2	32356.0		3	32349.5				2X225.0
			225.1						
1	1	32130.9					2	32117.1	
	Mean differences 223.1			223.1			223.4		

TABLE III—Continued

m	SERIES 23			SERIES 22			SERIES 21		
	I	N	D	I	N	D	I	N	D
23									
22									
21									
20									
19									
18	7	35907.5	(2784.93) 224						
17	5	35683	224	5	35673.3	(2803.22) 222.2			
16	9	35459.4	221.5	9	35451.1	222.8	9	35446.9	(2821.12) 223.4
15	8	35237.9	225.1	8	35228.3	222	7	35223.5	223
14	8	35012.8	223.3	8	35006	223	8	35001	225
13	8	34789.5	223.7	9	34783.2	222.1	8	34776.0	222.5
12	6	34565.8		5	34561.1	220.9	6	34553.5	
11		2×222.0		5	34340.2	223		2×221.9	
10	5	34121.7	222.3	5	34117	222	4	34109.7	
9	5	33899.4		5	33895.1	222.3		2×222.8	
8				5	33672.8		3	33664.2	222.4
7		3×223.2			2×224.4		2	33441.8	222.9
6	3	33229.8	225.1	3	33224.0		2	33218.9	
5	5	33004.7	222.9		2×223.5			2×224.3	
4	4	32781.8	221.3	5	32777		4	32770.3	
3	4	32560.5							
2		2×224.7							
1	2	32111.2							
	Mean differences 223.3			222.8			223.0		
	SERIES 20			SERIES 19			SERIES 18		
23									
22									
21				7	36554.3	(2735.66)			
20					3×223.1				
19	4	36113.1	(2769.08) 224.2						
18	6	35888.9	222.9	6	35884.9	224.8	7	35880.6	(2787.02)
17	5	35666.0	224.2	5	35660.1	221.5			

TABLE III—Continued

m	SERIES 20			SERIES 19			SERIES 18		
	I	N	D	I	N	D	I	N	D
16	9	35441.8		9	35438.6				3×224.3
			222.2			224.7			
15	7	35219.6		6	35213.9		7	35207.7	
						223.7			222.1
14				8	34990.2		8	34985.6	
13			3×223.3			2×222.1			
12	7	34549.7		7	34546.0				4×222.6
			223.1			223.6			
11	5	34326.6		5	34322.4				
10							4	34095.4	
9									2×222.3
8			5×222.7			5×223.1	1	33650.8	
7									
6	2	33213.0		2	33206.9				7×224
5			2×222.7			2×223.0			
4	5	32767.7		4	32760.8				
3						3×223			
2				2	32091		1	32083	
1									
	Mean differences 223.0			223.1			223.4		
m	SERIES 17			SERIES 16			SERIES 15		
	I	N	D	I	N	D	I	N	D
23									
22									
21				7	36541.6	(2736.61)	6	36530.0	(2737.48)
						223.3			224.6
20	2	36324.8	(2752.94)	3	36318.3		4	36305	
19			2×223.9			2×223.4			2×223
18	6	35877.0		8	35871.6		7	35859.5	
			223.3			223.5			222.1
17	6	35653.7		6	35648.1		6	35637.4	
									223.6
16			2×224.6			2×224.6	6	35413.8	
									222.5
15	7	35204.4		7	35198.9		7	35191.3	
			223.3			223.2			221.7
14	8	34981.1		8	34975.7		7	34969.6	
			221.7			224.8			223.4
13	6	34759.4		5	34750.9		6	34746.2	
									222.4
12			2×222.5			2×224.2	7	34523.8	
11	4	34314		4	34302.4				2×224.3
			224.7						
10	4	34089.0					3	34075.2	
9						3×221.8			2×222.8
8			4×222.9	1	33637.1		1	33629.6	
7						2×223.8			2×223.1
6	2	33197.3		2	33189.6		2	33183.4	
									221
5			2×225			2×223.0	3	32962	

TABLE III—Continued

m	SERIES 17			SERIES 16			SERIES 15		
	I	N	D	I	N	D	I	N	D
4	3	32747		2	32743.6		3	32517.0	2 × 222.5
3									
2			3 × 223			3 × 223			2 × 223.5
1	1	32079		1	32074		1	32070	
Mean differences 223.5				223.4			223.0		
m	SERIES 14			SERIES 13			SERIES 12		
	I	N	D	I	N	D	I	N	D
23									
22									
21	6	36724.0	(2737.86)						
20				4	36297.4	(2755.02)			
19			3 × 223.0			2 × 224.4			
18	9	35855.7		9	35848.7				
			223.5			220.0			
17	6	35632.2		7	35627.8		7	35622.9	(2807.18)
			223.4			222.6			221.5
16	6	35408.8		7	35405.2		7	35401.4	
			223.1			224.4			
15	7	35185.7		7	35180.8				2 × 224.2
			221.0			221.5			
14	7	34964.7		7	34959.3		7	34953.1	
			222.6						
13	7	34742.1							
12			2 × 225			3 × 224.0			3 × 223.1
11	5	34292		6	34287.3		7	34283.9	
			222			221.8			
10	4	34070.3		4	34065.5				
			221			222			
9	3	33849		3	33844				3 × 222.6
						223			
8			2 × 224	1	33621.1		1	33616	
7	2	33402							2 × 223.1
			222						
6	2	33179.8				3 × 223	2	33169.5	
									223
5			2 × 222.0	2	32952		3	32947	
						222			224
4	2	32735.8		2	32729.9		2	32723	
3									
2									
1									
Mean differences 222.9				223.0			223.1		
m	SERIES 11			SERIES 10			SERIES 9		
	I	N	D	I	N	D	I	N	D
23									
22				8	36733.2	(2722.33)			
21	6	36514.9	(2738.61)						
20									
19			3 × 224.5			4 × 224.6			

TABLE III—Continued

m	SERIES 11			SERIES 10			SERIES 9		
	I	N	D	I	N	D	I	N	D
18	9	35841.5		8	35834.8		8	35828.7	(2791.06)
			223.4			222.6			221.4
17	7	35618.1		6	35612.2		6	35607.3	
			222.6			221.1			221.7
16	7	35395.5		7	35391.1		7	35385.6	
			223.2			224.4			223.7
15	8	35172.3		8	35166.7		8	35161.9	
			223.8			224.6			
14	7	34948.5		7	34942.1				
			224.6						
13	5	34723.9							4×222.2
			223.1						
12	6	34500.8							
			223.8						
11	8	34277.0					8	34273.1	
			221.5						
10	5	34055.5							2×222.7
			221.6						
9	3	33833.9				10×222.6	4	33827.7	
									224.3
8							1	33603.4	
7			3×223.1						2×222.7
6	1	33164.5					1	33158.0	
									2×223.8
5							2	32710.2	
4				2	32715.9				224
						2×225.1	3	32486	
3									
2				1/2	32265.7				
1									
		Mean differences	223.4			223.4			222.9
m	SERIES 8			SERIES 7			SERIES 6		
	I	N	D	I	N	D	I	N	D
23							7	36933	(2707.6)
22									2×224
21	6	36497.4	(2739.92)	6	36490.2	(2740.46)	6	36485	
20									
19			3×224.7			3×223.7			3×223.3
18	7	35823.2		7	35818.9		7	35815.3	
						222.8			223.8
17			2×222.5	6	35596.1		6	35591.5	
						222.4			222.8
16	7	35378.2		6	35373.7		6	35368.7	
			221.4			221.1			222.6
15	8	35156.8		8	35152.6		7	35146.1	
			221.8						222.8
14	6	34935.0					6	34923.3	
13						4×223.4			
12			3×222.9						3×223.0
11	9	34266.4		8	34258.9		7	34254.2	
						223.0			223.3
10			2×223.0	10	34035.9		10	34030.9	
						223.6			223.0

TABLE III—Continued

<i>m</i>	SERIES 8			SERIES 7			SERIES 6		
	I	N	D	I	N	D	I	N	D
9	5	33820.4		7	33812.3		7	33807.9	
8									
7			3×223.4			4×223			4×223
6	2	33150.1	224						
5	2	32926	222	2	32921	224	2	32916	
4	2	32704.0		2	32697				2×223
3							3	32470.3	224
2							3	32246	
1									
Mean differences 223.1				223.1			223.2		
<i>m</i>	SERIES 5			SERIES 4			SERIES 3		
	I	N	D	I	N	D	I	N	D
23									
22									
21				6	36480.7	(2741.18)	5	36474.4	(2741.65)
20									
19						4×224			3×223.8
18	7	35807.9	(2702.68) 221.6				7	35802.9	224.8
17	7	35586.3		7	35583	222	8	35578.1	222.4
16			2×222.2	6	35361.2	223.0	6	35355.7	222.5
15	7	35142.0		7	35138.2	220.0	7	35133.2	
14				5	34916.0				2×222.0
13			4×222.8			2×223.4	3	34689.3	224.1
12				9	34460.1	224.6	8	34465.2	225.1
11	7	34250.6		8	34244.5		8	34240.1	222.2
10			2×223.2			2×222.2	10	34017.9	222.6
9	8	33804.1		8	33800.1		8	33795.3	221.9
8			2×224			2×224.1	8	33573.4	2×224
7	5	33356	223	7	33351.9				
6	2	33133	222				8	33125.4	225
5	2	32911	2×223				3	32900	
4									
3	3	32464.3							
2									
1									
Mean differences 222.9				223.5			223.4		

TABLE III—Continued

<i>m</i>	SERIES 2			SERIES 1		
	I	N	D	I	N	D
23						
22						
21	6	36470	(2742.0)			
20						
19			3 × 224			
18	7	35799.1	224.9			
17	7	35574.2	224.0			
16	6	35350.2	223.2			
15	8	35127.0	222			
14	7	34905	2 × 222.5			
13				4	34676.7	(2883.79)
12	8	34459.5	223.4			2 × 221.9
11	8	34236.1	223.2	9	34233.0	224
10	9	34012.9	2 × 223.0	9	34009	223
9				9	33785.6	2 × 223.6
8	9	33566.8	223			
7	9	33344	223	9	33338.3	221.2
6	8	33120.7		9	33117.1	223.1
5			3 × 223	4	32894.0	2 × 223.9
4				4	32446.2	
3	3	32452	225			
2	½	32227				
1						
Mean differences 223.3				223.1		

It is obvious from Table III that equality of the observed intensities is not rigidly held in the series; there is too great a probability of error between the observed and actual values to make strict conformity to such a condition needful.

TABLE IV

I	N	D	I	N	I	N	I	N	I	N
9	34000.0		7	36685.9	6	35644.4	9	34385	3	33450.8
		225.1								
10	33774.9		5	36656.4	10	35473.9	5	34336.5	4	33260.7
		2 × 223.0								
10	33328.8		5	36649.4	9	35455.0	9	34226.5	9	33112.8
		2 × 224.8								
10	32879.3		5	36643.1	6	35418.0	6	34134.8	7	33037.4
		2 × 222.8								
5	32433.7		8	36507	8	35382.8	5	34046	5	32999
			6	36312.0	9	35276.0	9	34024	3	32886
			5	36206.0	8	35233.7	8	33930.2	8	32633
	Mean differ. 223.7		5	36013	3	34680	5	33909.8	2	32573.1
			7	35985.3	9	34606.1	9	33791.8	3	32478
			7	35903.8	9	34597.1	5	33689		
			8	35864.9	9	34479.5	8	33577		

ERRORS

1. *In wave-lengths.*—The wave-lengths were determined by measurements made on the lines on two plates, six measurements of one plate and four of the other. The difference between the mean values of the wave-length of any one line obtained from the two plates is in many cases less than 0.1, in the majority of cases less than 0.15, although in some cases this difference amounts to 0.2 Å. The following are examples of the mean values of wave-lengths obtained from the two plates:

Plate 26	Plate 28	Plate 26	Plate 28
2811.85	2811.91	2916.83	2916.82
2812.27	2812.28	2917.39	2917.44
2812.60	2812.72	2918.20	2918.41
2813.16	2813.23	2918.87	2919.01
2813.52	2813.68	2919.66	2919.66
2814.23	2814.10	2920.09	2920.28
2814.55	2814.58	2920.89	2920.88
2814.70	2814.90	2921.46	2921.45
2815.37	2815.33	2922.24	2922.17
2815.77	2815.82	2922.87	2922.91

2. *In wave-numbers.*—Let

N = true wave-number,
 λ = true wave-length,
 ν = error in N ,
 ϵ = error in λ .

Then

$$\begin{aligned} N - \nu &= \frac{1 \times 10^8}{\lambda + e}, \\ &= N - \frac{e \times 10^8}{\lambda^2}. \end{aligned}$$

For the upper limit in the spectrum, $\lambda = 3200$, hence $\nu = 10e$; for the lower limit $\lambda = 2700$, hence $\nu = 13e$; thus an error of 0.1 \AA in λ corresponds to an error of 1 or 1.3 in N . Some of the lines, whose wave-lengths have been given to the second place of decimals and their wave-numbers to the first place, may not be correct to 1 in those places, but they have been left to the nearest calculated value there when the probable error in the mean value of the wave-length was only about 0.03. This was done because giving the wave-numbers to the units place only would have frequently doubled the error in the first differences. The close agreement with one another of the mean values of the common differences of the arithmetical progressions seems to justify this course in many cases. For lines with larger probable errors, wave-lengths are given only to the first place of decimals and wave-numbers to the units place.

3. *In intensity*.—The want of accuracy in estimation by eye of the relative intensities of lines is well recognized. The difficulty in such estimation increases greatly with the number of lines to be observed, which here amounts to nearly 600. Further, errors must be present in the estimated intensity of absorption of those lines, which occur very near a broad metallic line strong enough to be transmitted through the gas. For example, the intensity of wave-number 33538.4 would most probably be represented by a higher number if full allowance were made for the increased intensity of the background due to the breadth of the metallic line 2980.79. Fig. 1 shows the position of some of the metallic lines transmitted; the absence of absorption lines at some of these places suggests that they are hidden by the metallic lines. The plates show several metal lines broadened by the capacity required to produce the continuous spectrum.

SIMILAR REGULARITY IN OTHER SPECTRA

1. *In emission spectra*.—Equal first differences in wave-numbers have been found by: Ames¹ in zinc and cadmium between the

¹ *Philosophical Magazine* (5), 30, 33-48, 1890.

frequencies of the first and second and between the second and third lines of most of the triplets; Kayser and Runge¹ in tin, lead, arsenic, antimony, and bismuth; Rydberg in copper² and in the red spectrum of argon;³ Kayser⁴ in the elements of the platinum group; Snyder⁵ in rhodium, in the lines measured by Kayser; Olmsted⁶ in the oblique series of barium, strontium, and calcium; Messerschmitt⁷ in the heads of those bands of selenium which lie in the ultra-violet region. In these spectra, with the exception of the last two named, the constant first difference is different for different groups of lines of the same element.

In contrast with the above spectra, Professor Wood⁸ has found in the resonance spectrum of sodium vapor series of lines having equidistant wave-lengths.

2. *In absorption spectra.*—Friedrichs⁹ found in the absorption spectrum of Mn_2Cl_7 two kinds of bands, arranged in groups, those of one kind strong, the other weak, the groups alternating with each other. A constant first difference appeared between the wave-numbers of the edges of the first bands of the strong groups; also between those of the weak groups, as follows:

STRONG GROUP		WEAK GROUP	
N	ΔN	N	ΔN
1896	76	1919	76
1972		1995	
2048		2071	
2124	76	74	74
2201	77		
2278	77		

¹ "Ueber die Spectren der Elemente," 7 Abschrift, *Abhandl. Berl. Akad.*, 1894.

² *Astrophysical Journal*, **6**, 239-243, 1897.

³ *Ibid.*, **6**, 338-348, 1897.

⁴ "Ueber die Bogenspectren der Elemente der Platingruppe," *Abhandl. Berl. Akad.*, 1897.

⁵ *Astrophysical Journal*, **14**, 179-180, 1901.

⁶ *Zeitschrift für wissenschaftliche Photographie*, **4**, 255-291, 293-333, 1906.

⁷ *Ibid.*, **5**, 249-278, 1907.

⁸ *Astrophysical Journal*, **30**, 339, 1909.

⁹ *Zeitschrift für wissenschaftliche Photographie*, **3**, 154-166, 1905.

Here the first differences are approximately the same for the two groups.

Another example of this structure in absorption spectra is in that of the vapor of paraxylene, found by Mies.¹ The approximately constant first differences are between the wave-numbers of the heads of bands, which are not resolved into lines; hence, as might be expected, there are comparatively large variations in the constants.

In an earlier work by Käbitz² on the spectrum of the vapor of CrO_2Cl_2 this simple structure can be found. He found five series of *Absorptionstreifen* (broad lines) in this spectrum; his values of the wave-lengths with their first and second differences are quoted below in Table V. The writer has calculated their wave-numbers and placed them in columns parallel with those containing the wave-lengths. The first four columns are quoted from Käbitz' paper; for the fifth and sixth columns the present writer is responsible. n denotes the number of the line in the spectrum.

It is obvious from the fifth and sixth columns of this table that the *first* differences of the wave-numbers of these series are approximately equal; further, that this constant difference, namely 135, is approximately the same for all the series. Hence this spectrum does not obey Deslandres' third law.

TABLE V

SERIES I. PRINCIPAL SERIES					
n	λ	D_1	D_2	N	ΔN
3	5846.5			17104	
8	5800.2	46.3	1.1	17241	137
13	5755.0	45.2	0.5	17376	135
18	5710.3	44.7	0.9	17512	136
23	5666.5	43.8	0.4	17648	136
28	5623.1	43.4	2.1	17784	136
33	5581.8	41.3		17915	131

Mean $\Delta N = 135$

¹ *Zeitschrift für wissenschaftliche Photographie*, 7, 357-368, 1909.

² *Ueber die Absorptionsspectra der Chlorsäuren*, Dissertation, Bonn, 1904.

TABLE V—Continued

SERIES II. SUBORDINATE SERIES I						SERIES III. SUBORDINATE SERIES II					
<i>n</i>	λ	D_1	D_2	<i>N</i>	ΔN	<i>n</i>	λ	D_1	D_2	<i>N</i>	ΔN
4	5837.1			17132		5	5827.5			17160	
		45.3			134			46.1			137
9	5791.8		0.1	17266		10	5781.4		1.2	17297	
		45.2			136			44.9			135
14	5746.6		1.0	17402		15	5736.5		0.6	17432	
		44.2			135			44.3			136
19	5702.4		0.1	17537		20	5692.2		0.5	17568	
		44.1			136			43.8			136
24	5658.3		1.4	17673		25	5648.4		2.4?	17704	
		42.6			134			41.4			131
29	5615.8		1.3	17807		30	5607.0		0.6	17835	
		41.3			132			40.8			127
34	5574.4			17939		35	5567.2			17962	

Mean $\Delta N = 135$ (Omitting the last) Mean $\Delta N = 135$

SERIES IV. SUBORDINATE SERIES III						SERIES V. SUBORDINATE SERIES IV					
<i>n</i>	λ	D_1	D_2	<i>N</i>	ΔN	<i>n</i>	λ	D_1	D_2	<i>N</i>	ΔN
1	5865.9			17048		2	5855.3			17079	
		46.6			136			46.1			135
6	5819.3		0.4	17184		7	5809.2		0.8	17214	
		46.2			138			45.3			135
11	5773.1		1.3	17322		12	5763.9		0.9	17349	
		44.9			135			44.4			135
16	5728.2		0.5	17457		17	5719.5		0.7	17484	
		44.4			137			43.7			135
21	5683.8		0.9	17594		22	5675.8		0.9	17619	
		43.5			136			42.8			134
26	5640.3		0.6	17730		27	5633.0		0.8	17753	
		42.7			135			42.0			133
31	5597.6			17865		32	5591.0			17886	

Mean $\Delta N = 136$ Mean $\Delta N = 135$

CONCLUSION

The spectra of SO_2 and CrO_2Cl_2 exhibit a very simple and definite structure, which is built up of a number of series of lines characterized by equidistant frequencies, this equal distance having approximately the same value in every series; for SO_2 it is 223, for CrO_2Cl_2 it is 135. Thus the different members of the structure are simple in themselves,

being expressed by arithmetical progressions, whose common difference is the difference in frequency. These members are united into a regular structure by the simple tie that the mean frequency difference of every series is approximately the same.

BRYN MAWR COLLEGE
PENNSYLVANIA
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THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS AND NON-AQUEOUS SOLUTIONS

By FRANK L. COOPER

Introduction.—There is perhaps no other investigation connected with molecular vibrations which is of greater interest than that which endeavors to trace the connection of the spectrum of an element and that of its compounds.

It was first considered that an element preserved its spectrum when entering into combination, so that, for instance, the oxide of a metal would show only the metallic lines except in so far as oxygen lines might be visible. This idea had to be given up, but the absorption spectra of liquids were considered at first to be evidence in favor of the assumption of permanence of the spectrum of an element when combined with others. A large amount of work has already been done on the absorption of light by solutions, but there still remains some doubt regarding the nature of the "absorber," and it was for this reason that the present investigation was undertaken. Before it was entirely completed, however, a monograph by Jones and Anderson entitled "The Absorption Spectra of Solutions"¹ appeared, in which the authors arrived at some of the conclusions which were inferred from the present investigation. Since the method of investigation in the two cases is not entirely the same, it was thought desirable to give the results of the present investigation as confirming the conclusions of Jones and Anderson.

Before taking up in detail the work that is here recorded, a brief discussion of some of the more important work in the same field seems desirable.

Historical review.—We owe the first systematic investigation of the absorption spectra of solutions to Gladstone,² who examined the absorption of solutions of salts, each constituent of which was colored. He came to the conclusion that generally, but not invariably, the following law holds good: "When an acid and a base combine, each

¹ *Carnegie Institution of Washington, Publication No. 110, 1909.*

² *Phil. Mag.*, 14, 418, 1857.

of which has a different influence on the waves of light, a solution of the resulting salt will transmit only that light which is not absorbed by either, or, in other words, which is transmitted by both." Thus, for instance, chromic acid in solution cuts off the more refrangible half of the spectrum, transmitting only the blue near F, in dilute solutions, while the less refrangible part is transmitted perfectly. The characteristic absorption of chromic acid remains when the acid is combined with such metals as copper, nickel, uranium, potassium, and chromium, but the salts formed by combination with copper and nickel also show their own influence, when combined with chromic or other acids, by absorbing part of the red end of the spectrum. Potassium salts are colorless when combined with colorless acids and, therefore, potassium chromate shows the same spectrum as chromic acid. Chromate of chromium forms an exception to the rule, for, although the absorption peculiar to chromic acid exists, the absorption visible in ordinary chromium salts does not appear. Gladstone also examined the effect of chlorine, bromine, and iodine when combined with different metals. The bromides of gold, palladium, potassium, and platinum gave spectra which are identical with the spectrum of bromine water; the same applies to a concentrated solution of bromide of copper which, in addition, shows the red absorption characteristic of copper. Similar results were obtained with the chlorides and iodides.

In pointing out that it is generally, though not universally, true that a base or an acid retains its absorptive properties in different combinations, Gladstone calls attention to the exception of ferric ferrocyanide which, when dissolved in oxalic acid, transmits blue light, although the same light is generally absorbed both by ferrocyanides and by ferric salts.

Babo¹ observed that cobalt chloride in concentrated solution was colored blue by absolute alcohol at ordinary temperatures. At more elevated temperatures a few drops of alcohol were sufficient to produce a blue color. A solution of calcium chloride or magnesium chloride readily changes the color of cobalt chloride to blue, especially at the boiling-points of the solutions. A concentrated solution of

¹ *Ber. über der Verhandl. der Gesell. für Beford. der Naturm. zu Freiburg i. B.*, No. 17, 283, 1857; *Jahresber.*, p. 72, 1857.

zinc chloride, on the other hand, gave only red color with cobalt chloride, even when the mixture was warm. Babo concluded that the change of color was due to the formation of a double salt, and that whenever there was a transformation from a reddish to a blue color there was hydration of the cobalt salt.

Erhard¹ studied the absorption spectra of some salts in which chromium plays the rôle of a base. He found that as a general rule these salts absorbed the yellow end of the spectrum transmitting the blue; the exact position of the maximum of absorption, however, and the intensity of the absorption band varied considerably with different salts, and even for the same salt at different temperatures, and the results were complicated by the fact that heating the salts produced a permanent alteration in the absorption. The insoluble chloride of chromium showed a behavior differing from the other chromium salts. There was, however, a general resemblance in the absorption of different chromium salts but no identity.

Nitric acid and the nitrates of transparent bases such as potassium, sodium, and ammonia showed spectra according to Soret² which were not only qualitatively, but also quantitatively identical; that is to say, a given quantity of nitric acid in solution gives a characteristic absorption band of exactly the same width and intensity whether by itself or combined with a transparent base. It also showed a continuous absorption at the most refrangible side, beginning with each of the salts mentioned, at exactly the same position in the spectrum. The etheral nitrates,³ however, gave different results.

In most of the cases hitherto discussed, the characteristic absorption of the substance under examination extended over a considerable range; the substance either absorbed a large part of the light or at least showed absorption bands which were broad and increased considerably in width with increase of concentration. When, however, absorption bands become narrower and more definite, so that they can be examined under high dispersion, their behavior under different circumstances becomes more interesting, for we can trace smaller differences and more minute changes.

¹ Inaugural Dissertation, Freiburg, without date.

² *Bibliothèque Universelle Arch. Sc. Pb.*, 61, 322, 1878.

³ *British Assoc. Rep.*, p. 55, 1880.

It was Bunsen¹ who first showed that such small changes do occur. While studying different salts of neodymium, he found that although all the salts showed spectra so nearly identical that, with the ordinary one-prism spectroscope, they could easily be mistaken for each other, higher dispersion revealed some very interesting and characteristic changes. His conclusions are best quoted in his own words:

Very remarkable and noteworthy are the small alterations in position which occur in the minima of brightness in the didymium spectrum, depending upon the nature of the compound in which the metal occurs. These changes are too minute to be seen with the small, though seen with the large, instrument. I have as yet investigated them completely only in the case of three didymium salts, viz., the chloride, sulphate, and acetate. It is, however, more than probable that the same phenomena will also be found to occur with the absorption spectra of other crystals of didymium salts, and perhaps may be exhibited with the luminous spectra of the oxide and other compounds of didymium. The atomic weight of didymium chloride is 95.9, and that of the anhydrous acetate is 106.9. It will be noticed that all the groups of bands in the case of the salts under examination approach the red end of the spectrum in the order of their increasing atomic weight.

These differences here noticed in the absorption spectra of different didymium compounds cannot, in our present complete state of ignorance of any general theory for the absorption of light in absorbing media, be connected with other phenomena. They remind one of the slight and gradual alterations in pitch which the notes from a vibrating elastic rod undergo when the rod is weighted, or of the change of tone which an organ pipe exhibits when the tube is lengthened.

Some interesting cases of the shifting of bands in different compounds of the same metal have been found by Russell,² who subjected the cobalt salts to a very careful and most instructive examination. He worked with a fused chloride, with its solution in concentrated hydrochloric acid, and with its solution in various alcohols. He showed that the spectrum in the concentrated acid was very similar to that of the fused salt, the bands being displaced a little toward the blue. The spectrum of cobalt chloride, when dissolved in the various alcohols and in glycerol, were practically the same, independent of the nature of the solvent.

Russell also worked with aqueous solutions of different concentrations, studying their absorption spectra and observing the effect of temperature-changes. He concluded that the color of the aqueous solutions was due to the presence of hydrates.

¹ *Phil. Mag.* (4), 32, 177, 1866.

² *Proc. Roy. Soc.*, 37, 258, 1881.

W. H. Hartley,¹ in his elaborate investigation of absorption spectra, has included a number of salts of cobalt. His experimental work consisted in observing and photographing the spectra of a large number of solutions of chlorides, bromides, iodides, nitrates, etc., of a fairly large number of metals, including cobalt. Some of the more interesting and important conclusions at which he arrived, stated in nearly his own words, are the following: When a definite crystalline hydrate is dissolved in a non-aqueous solvent, upon which it does not act chemically, the molecules of the salt remain unchanged in chemical composition.

In a series of anhydrous salts which do not form definite crystalline hydrates, the effect of rise in temperature up to 100° C. does not produce any alteration in their absorption spectra other than that which results with substances which undergo no chemical change with such rise in temperature. The change in question is usually an increase in the intensity of the absorption, or a slight widening of the absorption bands. Crystallized hydrated salts dissolved in a minimum amount of water at 20° C. undergo dissociation when the temperature is raised. The extent of the dissociation may proceed as far as complete dehydration of the compounds, so that more or less of the anhydrous salt may be formed in the solution.

The most stable compound that can exist in a saturated solution at 16° C. or 20° C., has not always the same composition as the molecule of the crystallized solid at the same temperature, since the solid may undergo a partial dissociation from its water of crystallization when the molecule enters into solution. When a saturated solution of a colored salt suffers a great change in color or any remarkable change in its absorption spectrum upon dilution, the dilution is always accompanied by a marked evolution of heat.

Hartley² closes his paper on "The Absorption Spectra of Metallic Nitrates" with the following significant paragraph, as quoted by Jones and Anderson:

The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound

¹ *Trans. Roy. Dub. Soc.* (2), 7, 253-312, 1900; *Jour. Chem. Soc.*, 81, 571, 1902; 83, 221, 1903.

² *Jour. Chem. Soc.*, 83, 245, 1903.

into ions, but only a dissolution of such a character that the molecule is shown to consist of two parts, the movements of one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis, or by static electricity, and in some instances by photographic action.

Donnan and Bassett,¹ working with cobalt salts, came to the conclusion that the blue color of solutions of cobalt salts is due to the formation of complex anions containing cobalt.

Hartley² calls attention to certain inaccuracies in the above paper. It is not at all certain that, when hydrochloric acid is added to a solution of cobalt chloride, the blue color is due to the same cause as when an aqueous solution is heated. Indeed the absorption spectra in the two cases are quite different. Hartley points out further that the color of hot aqueous solutions was not supposed to be due to the anhydrous cobalt chloride, but to the dihydrate. Again, the spectra of a solution of cobalt chloride saturated at 20°, and taken at the temperatures 23°, 33°, 43°, 53°, 73°, and 93° C., are all quite different from the cobalt chloride to which hydrochloric acid had been added.

Of the more recent work, that of Jones and Uhler³ is very important. They worked with aqueous solutions of copper and cobalt salts, to which some dehydrating agent was added; and also with non-aqueous solutions of these salts to which water was added.

They found that in all cases where the ion would be expected to be hydrated the most, the bands were the narrowest.

Jones and Strong,⁴ working with salts of potassium and uranium, found that the absorption bands of uranyl nitrate in water are all farther toward the violet than for any other uranyl salt investigated, or for uranyl nitrate in other solvents.

THE PRESENT INVESTIGATION

In the present investigation, two entirely distinct methods have been used. In the first method the spectrum of the salt was examined

¹ *Jour. Chem. Soc. (London)*, **81**, 939, 1902.

² *Ibid.*, **83**, 401, 1903.

³ *Carnegie Institution of Washington, Publication No. 60*, 1907.

⁴ *Proceedings Amer. Phil. Soc.*, **48**, No. 192, 1909.

visually with a spectroscope and a quartz spectrograph and also photographed by means of a large spectrograph, while the condition of the salt remained the same. By the other method, the changes in the absorption spectrum of the solution were studied with both a spectroscope and a quartz spectrograph, while a chemical change was taking place. So in the first method the condition of the substance was the same throughout the investigation, while in the second case the condition was slowly varying.

Apparatus.—Three spectroscopes were used in this work; the first, which we will designate as the small spectroscope, consisted of one 60° prism; the second had six 60° prisms through each of which the light was made to pass twice. The third spectroscope was of the direct-reading type and was obtained from Hilger of London. A description of this form of instrument has been given by Jones and Uhler.¹ The spectrograph consisted of a plane Rowland grating of about 14,000 lines to the inch. The light after passing through the slit was rendered parallel by a condensing lens, and after striking the grating it was brought to a focus at the camera by means of a second lens, each lens having a focal length of about two and a half feet. The whole apparatus was inclosed in a light-tight box and rested upon a steel frame in the bottom of the box.

Through the courtesy of Professor H. A. Bumstead of the Sloane Physical Laboratory, it was also possible, for part of the work, to use the smaller Rowland concave grating belonging to that laboratory. This grating has 14,000 lines to the inch and is of 11 feet radius of curvature.

Sources of light.—For wave-lengths between the extreme red and below about 0.326μ the Nernst glower was used. These were 220-volt D.C. glowers carrying a current of 0.5 of an ampere. A variable resistance was placed in the circuit to maintain a constant current. For wave-lengths between the strong ultra-violet of the Nernst glower and the extreme ultra-violet, the arc with Norway iron electrodes was used. It was also used as the source of light when working with the concave grating.

Photographic material, etc.—The plates used were the "panchromatic" plates made by the Wratten & Wainright Co., of Croydon,

¹ *Carnegie Institution of Washington, Publication No. 60, p. 170, 1907.*

England. These plates were of very thin glass and were found to be very uniformly sensitive to light of all wave-lengths, from the very short wave to about $\lambda 7400$. Besides, as a check on the results, considerable work was done, making use of Seed's Gilt Edge plates No. 27, Cramer's Trichromatic, and also the Standard Orthonon plates. The developer used was a hydroquinone solution made up according to Jewell's¹ formula.

Solutions.—The solutions were made up in the following manner, which is the same method used by Jones and Uhler:² A chosen volume of mother-solution of a colored salt was measured out from a burette into a measuring flask of known capacity. The portion of the solution in the flask was then diluted by the addition of pure water until the volume of the resulting homogeneous liquid was exactly equal to the fixed capacity of the flask. The concentrations will always be expressed as multiples of normal. The term "normal" will be used to mean gram-molecular normal, i.e., a liter of solution which contains just as many grams of anhydrous salt as there are units in the number expressing the molecular weight of the salt is defined as normal.

Cells.—There were three cells used in this work, each of which was made with quartz-plate sides. They were constructed so that the length of the absorbing layer would be 1 cm, 2 cm, or 4 cm, according to the cell used.

RESULTS—FIRST METHOD

Solutions of cobalt salts.—Several salts of cobalt have been examined in this investigation. Plates have been obtained for aqueous solutions of cobalt chloride, bromide, iodide, sulphate, nitrate, nitrite, and acetate. These salts were also studied when dissolved in absolute ethyl alcohol, absolute methyl alcohol, and glycerine, also qualitatively when the salts were dissolved in various acids; some of the oxygen salts, however, were not absolutely anhydrous.

The concentrations of the solutions used in making the spectrograms varied from 2.0 normal to 0.1 normal, each of the solutions

¹ *Astrophysical Journal*, **11**, 240-243, 1900.

² *Carnegie Institution of Washington, Publication No. 60*, 1907.

being examined with each cell so that the lengths of the absorbing layer were 1 cm, 2 cm, and 4 cm.

The solutions were examined with both the Hilger spectroscope and the quartz spectrograph as well as with the grating spectrograph. Whenever the absorption spectra of two aqueous solutions, for example, were compared, it was for corresponding concentrations. In making the exposures with the spectrograph, the light of both the Nernst glower and the iron-arc was used, although most of the spectrograms were obtained with the Nernst lamp. In studying the ultra-violet region of the spectrum with the quartz spectrograph, the light from the iron-arc was used.

Cobalt chloride in water.—Commencing with the smallest and increasing the concentration, the absorption bands appeared in the following order: There were two regions of absorption in the ultra-violet, one in the extreme ultra-violet, and the other near the visible spectrum at about λ 3300. As the concentration increased, these two bands came together, appearing as one band and extended toward the red to about λ 4000.

The second band to appear was in the green, center at about λ 5200, although this band appeared about the same time as the band at λ 3300. With increasing concentration, this band widened, extending from λ 4730 to λ 5340. In very concentrated solutions, a faint band appeared at about λ 6090 and also one in the red extending from λ 6750 to λ 6900. With the smaller concentrations, these last two bands could not be seen without increasing the length of the absorbing layer.

Cobalt bromide in water.—In this case as with the cobalt chloride solutions, the absorption bands in the extreme ultra-violet appeared first, although the solutions of cobalt bromide were more transparent in this part of the spectrum. The band which, with the chloride solution, extends from about λ 3000 to λ 4000 in very concentrated solutions was not present in the spectra of the bromide solutions.

The second band to appear was the strong band in the green. It first appeared at λ 5200, that is, at the same position in the spectrum as was found for the corresponding band in the green with the chloride.

The red band could not be seen in the more dilute solutions, but as the concentration was increased a faint band appeared with the center at about λ 7000.

Cobalt iodide in water.—Owing to the ease with which the iodide of cobalt dissociates, its absorption spectrum was more difficult to study. Several spectrograms have been obtained, however, which show the general nature of the spectrum, although they are not definite like those obtained for the chloride and bromide solutions.

The absorption spectra of these solutions were also examined carefully with the small spectroscope, the Hilger direct-reading spectroscope, and with the quartz spectrograph. It was impossible to determine the limit of transmission in the ultra-violet, but the band in the green was present, although its exact position was not determined.

There was also a very slight absorption in the red, but this band was farther toward the red end of the spectrum than with either the chloride or bromide. It should be said, however, that its position was determined from the ethyl alcohol and not from the water solution, and therefore would not be the position of the band in the aqueous solution, could it have been determined.

Cobalt sulphate in water.—The spectrum of the sulphate solutions differed from those of cobalt chloride, bromide, and iodide, in that they were entirely transparent in the red for all concentrations, as far as λ 7400. The dilute solutions were also quite transparent in the ultra-violet, but with increasing concentration the absorption in this region increased. As there were no sharp absorption bands in the ultra-violet, it was impossible to determine the exact limits of transmission in this region.

In the green there was strong absorption and the band was more intense. The center of the band was in about the same position in the spectrum as was found with the cobalt chloride and bromide solutions.

Cobalt nitrate in water.—The spectrograms, as well as the visual observations, showed two distinct regions of absorption, one in the green and the other in the ultra-violet. The center of the band in the green appeared to have moved toward the violet end of the spectrum, but this can be explained, in part at least, by the fact that the band did not widen symmetrically as the concentration of the solution increased. This explanation was confirmed by the visual observations with the Hilger spectroscope.

The absorption in the ultra-violet was probably due to two bands, although they were not resolved.

All the solutions transmitted the red as far as λ 7400, in this respect also being similar to the spectra of the solutions of cobalt sulphate.

Cobalt nitrite in water.—The work with cobalt nitrite was taken up especially to ascertain whether the spectra of the solutions of two salts, differing in composition only in the amount of oxygen contained, were similar. For this reason all the work was limited to the visible part of the spectrum.

By referring to Fig. 1 it will be seen that the spectra in the two cases are not the same. The spectrum of the nitrate shows only a band in the green, while the spectrum of the nitrite solution of the same concentration and length of absorbing layer, shows also a strong band in the blue and violet. It will be noticed, however, that the green band is in exactly the same position and is of the same width in the two spectra, showing that it must be due to the same kind of "absorber."

Cobalt acetate in water.—As was found with the solutions of cobalt nitrate and cobalt sulphate, there were also two regions of strong absorption with the solutions of cobalt acetate, one in the ultra-violet and another in the green. With the more dilute solutions, the limit of transmission was in the extreme ultra-violet, but the absorption band widened, extending farther toward the red end of the spectrum, as the concentration of the solution was increased.

The center of the band in the green appeared to change position slightly as the concentration of the solution changed, but this can be explained by the fact that the band did not widen symmetrically.

The solutions easily transmitted the yellow, orange, and the red as far as λ 7400.

Cobalt chloride in absolute ethyl alcohol.—The concentration of the solutions used varied from 0.10 to 0.01 normal, and the lengths of the absorbing layer were 1 cm, 2 cm, and 4 cm.

The sources of light used in making the spectrograms were the Nernst glower and the iron-arc. For the work with the quartz spectrograph the iron-arc was used as a source of light.

The solutions of cobalt chloride in ethyl alcohol showed a region of absorption in the extreme ultra-violet and also two other bands

which were nearer the visible spectrum, about λ 3100 and λ 3500 respectively. The last two bands could be seen only with the more concentrated solutions.

The green band could not be seen except in the solutions of greatest concentration and then only faintly. It was evident, however, that the center of the band was farther toward the red end of the spectrum than in the aqueous solutions, about λ 5270, as determined by the Hilger spectroscope.

The first bands to appear, even with the most dilute solutions, were the bands in the red, while with the water solutions these bands were the last to appear, and then only in very concentrated solutions. With the ethyl alcohol solutions, five bands could be seen, although two were very faint; a narrow band with its center at λ 5920, a band extending from λ 6020 to λ 6073, a stronger band with its edges at λ 6160 and λ 6235. There also appeared to be a faint band about λ 6420 and two stronger bands, one extending from λ 6520 to λ 6605 and the other from λ 6809 to λ 7000. As the concentration increased, the absorption bands in the red gradually widened and appeared as one broad band.

It is significant that, with the ethyl alcohol solutions, the absorption bands in the red appeared first, even in very dilute solutions, and the band in the green could not be seen except when the solution has become concentrated, while just the opposite was true in the case of aqueous solutions of cobalt chloride. Here the band in the green was strong even in very dilute solutions, but there was complete transmission in the red except in the most concentrated solutions.

Cobalt bromide in absolute ethyl alcohol.—The concentration of the solutions used was the same as in the case of cobalt chloride.

The absorption spectra of the solution of cobalt bromide in absolute ethyl alcohol showed strong absorption in the extreme ultraviolet, but the band extended farther toward the visible spectrum than in the case of the solutions of cobalt chloride in ethyl alcohol. The limit of transmission in the case of the cobalt bromide solutions was about λ 3000. There was no trace of any other absorption bands nearer the visible spectrum corresponding to those at about λ 3100 and λ 3500, which were found with cobalt chloride.

In the green there was no absorption except a trace with the longest

layers of the most concentrated solutions. The position of this band was approximately the same as with the chloride, although it was too faint to be determined accurately. The bands in the red were similar to those of the chloride, although they appeared to be shifted slightly toward longer wave-lengths.

In order to be sure that we were dealing with an entirely different set of bands from those obtained with the chloride, the spectrum of the chloride was superimposed upon that of the bromide. The light was first allowed to pass through two like cells each containing a solution of cobalt chloride of a definite concentration, and a spectrogram made. The same thing was repeated using cobalt bromide solution of the same concentration in both cells. Then a third spectrogram was made, one cell being filled with the cobalt chloride and the other with the solution of cobalt bromide. The absorption band, in the latter case, was the result of the superposition of the two entirely distinct bands, showing that the "absorber" in case of the cobalt chloride solution must be entirely distinct from that which produced the red absorption bands in the spectrum of cobalt bromide.

Cobalt iodide in absolute ethyl alcohol.—The concentration of the solutions was the same as used in the case of cobalt chloride and cobalt bromide, the length of absorbing layer and the sources of light also being the same.

The same difficulty was experienced with the ethyl alcohol solutions of cobalt iodide as with the water solutions. The spectrograms, however, showed an apparent displacement of the bands toward longer wave-lengths, but the bands were not sharp so it was impossible to determine the exact limits of transmission.

Cobalt nitrate in absolute ethyl alcohol.—The concentration of the solutions and all other conditions were the same as those used with the other cobalt salts. Since every condition was the same, their spectra could be compared, but it should be stated that the cobalt nitrate was not absolutely anhydrous. No attempt was made to determine the exact position of the absorption bands in the solution of cobalt nitrate, the object being simply to ascertain whether there were any bands in the red region of the spectrum. There was strong absorption in the ultra-violet, and also in the green, but no trace whatever of any absorption in the red could be found as far as λ 7400, either from

the spectrograms or from visual observations. The band in the green could not be seen except with concentrated solutions. Since there were no absorption bands in the red, the color of the solutions of cobalt nitrate in absolute ethyl alcohol, and also in water, was always red. The same thing was true of the solutions of cobalt sulphate, acetate, and nitrite, all of which had no absorption bands in the red.

Cobalt chloride in absolute methyl alcohol.—The concentration of the solutions used was varied from 0.30 to 0.01 normal, and the lengths of absorbing layer were 1 cm, 2 cm, and 4 cm. The sources of light used were the Nernst filament and the iron-arc. There was a region of absorption in the extreme ultra-violet in about the same position in the spectrum as in the case of the solution of cobalt chloride in ethyl alcohol. The two bands at λ 3100 and λ 3550 were also present in about the same position, although the exact position of these bands in the ultra-violet was not determined. There was strong absorption in the green. This band was more intense than with the ethyl alcohol solution and was displaced slightly toward the violet, the center of the band being at λ 5245. It was not as strong, however, as the corresponding band with the aqueous solutions of the same salt. The bands in the red were more sharply defined than in the ethyl alcohol solutions. There was a narrow band at λ 5915 which appeared only in the more concentrated solutions. There was, also, a band having its center at λ 6045, which was seen in the spectrum of the concentrated solutions. The third band was about 70 Ångström units in width, the center being at λ 6125. At λ 6418 there was another narrow band; besides, there were two others, one extending between the limits λ 6525 and λ 6650, and the other having its center at λ 6700.

Cobalt bromide in absolute methyl alcohol.—The absorption in the extreme ultra-violet was stronger than with the chloride dissolved in methyl alcohol. There were no bands, however, corresponding to the bands at λ 3100 and λ 3550 in the spectra of the chloride solutions.

The bands in the red were seen only in the spectra of very concentrated solutions.

Cobalt salts in other solvents.—Besides the work above recorded a qualitative study of cobalt salts dissolved in different acids was also

made. For this work the small spectroscope, the large spectroscope with six 60° prisms, and the quartz spectrograph were used.

No attempt was made to determine the exact position or to resolve the bands, but only to show that certain bands were characteristic of certain salts, although the condition of the salt itself might have been changed when dissolved in the acids. The results are recorded in the following table:

BANDS

Solution	Red	Orange	Green	Violet	Ultra-Violet
CoCl_2 in HCl	very intense	intense	faint	faint	faint
CoC_2O_4 in HCl	intense	faint	faint	faint	faint
CoCO_3 in HCl	intense	intense	faint	faint	faint
$\text{Co}(\text{NO}_3)_2$ in HCl	intense	faint	faint	very intense	faint
CoSO_4 in HCl	intense	intense	faint	faint	faint
CoCl_2 in $\text{HC}_2\text{H}_3\text{O}_2$	intense	faint	intense		intense
CoCO_3 in $\text{HC}_2\text{H}_3\text{O}_2$			intense		intense
$\text{Co}(\text{NO}_3)_2$ in $\text{HC}_2\text{H}_3\text{O}_2$	I.R.		intense	intense	intense
CoSO_4 in $\text{HC}_2\text{H}_3\text{O}_2$	I.R.		faint		intense
CoC_2O_4 in H_2SO_4			faint		intense
CoCO_3 in H_2SO_4			faint		intense

From the above table it will be seen that in every case where chlorine is present with the cobalt there is always strong absorption in the red, and in no case is there any absorption in the red if chlorine is not present.

In the case of cobalt nitrate and cobalt sulphate dissolved in acetic acid, a band appeared to approach from the infra-red and absorb part of the red. It is indicated in the table above by I.R. This absorption, however, could be observed only in the case of very concentrated solutions.

RESULTS—SECOND METHOD

Cobalt salt solutions.—For this part of the work both the small and the large spectroscope with six prisms were used. The method was as follows:

Light from a Nernst lamp was focused upon the slit of the spectroscope by means of a condensing lens, the light having passed through a cell 1 cm long containing absolute ethyl alcohol. Anhydrous cobalt chloride was then added to the alcohol until the bands in the red region of the spectrum became just distinctly visible. To

this solution of cobalt chloride in ethyl alcohol was then added a very small quantity of cobalt nitrate containing part of its water of crystallization. The spectrum was then examined carefully, and in a short time all the absorption bands in the red began to disappear slowly, while the band in the green gradually became stronger. This continued until all traces of any absorption in the red had vanished, although the band in the green grew more intense. A few drops of sulphuric acid were then added to the solution, and immediately the bands in the red reappeared.

It is reasonable to suppose that in the first case, that is, in the solution of anhydrous cobalt chloride in absolute ethyl alcohol, the "absorber" was the undissociated molecule of cobalt chloride, and that after the cobalt nitrate containing some water had been added to the solution, there was hydration and also dissociation of the cobalt chloride molecule sufficient to cause the absorption bands in the red to disappear. Since the chloride solution was made to such a concentration that the absorption bands in the red just appeared visible, the small amount of water present in the cobalt nitrate would be sufficient to cause this change in the spectrum.

From the odor and appearance of the solution it was suspected that oxidation of the chloride was slowly taking place. That such was probably the case was shown by the following experiment: The cell was cleaned and refilled with absolute ethyl alcohol. Then anhydrous cobalt chloride was added just sufficient to cause the absorption bands in the red to appear distinctly. A little cobalt nitrate containing some water of crystallization was added, as before, and the absorption bands in the red again began to disappear while the band in the green gradually became more intense. This continued until there was no trace of any absorption in the red region of the spectrum. The band in the green, however, continued to widen until the green, blue, and violet were absorbed, although the absorption in the violet was partly due to the bands in the ultra-violet region of the spectrum extending into the visible spectrum.

The solution was then allowed to stand for about fifteen hours and the spectrum examined at frequent intervals. After about five hours the spectrum appeared to be gradually changing, but this time it was neither the spectrum of cobalt chloride nor that of cobalt nitrate in

absolute ethyl alcohol. The band in the green gradually separated, and a strong narrow band appeared in the yellow with its center about λ 5850, and another band in the red at about λ 6020. The limit of transmission in the red was about λ 6070. There was also strong absorption in the violet and ultra-violet region as before. This spectrum is similar to that found by Russell for cobalt oxide.

The fact that this spectrum was not the same as either that given by the cobalt chloride or cobalt nitrate solutions is what would be expected if the "absorber" which produced the bands in the red was the undissociated molecule of the cobalt compound. Moreover, the absorption band in the green should always be present if the "absorber" which produced it was the cobalt atom or kation. That this was true was confirmed both by the spectrograms and by visual observations of the spectrum for every solution.

DISCUSSION OF THE RESULTS WITH COBALT SALTS

For the sake of comparing the spectra of the solutions of different salts of cobalt we have in Fig. 1 plotted the position of the bands in the spectrum of each salt studied. In some cases the edges of the bands are not sharply defined as indicated in Fig. 1, but the position of the center of each band was as represented. The limit of transmission in the ultra-violet, however, was not accurately determined.

The exact position of the absorption bands with the iodide solutions could not be definitely determined, although the spectrograms indicated a displacement of the bands toward the longer wave-lengths. The ultra-violet region of the spectrum of cobalt nitrite was not examined, as these solutions were studied only to ascertain whether the spectrum of a solution of cobalt nitrite differed from that of a solution of cobalt nitrate of the same concentration.

If we compare the spectra of the different salts in aqueous solutions, we find that the band in the green was always present, and in about the same position, especially in the dilute solutions. Moreover, the slight change in the position can easily be explained by the unsymmetrical widening of this band. This indicates that the band in the green must be produced by an "absorber" which is common to all of the salts, that is, that it must be due either to the cobalt atom or to the cobalt kation.

The view of Jones and Anderson that the "absorber" is the atom itself, and not the cobalt kation, is confirmed by the present work.

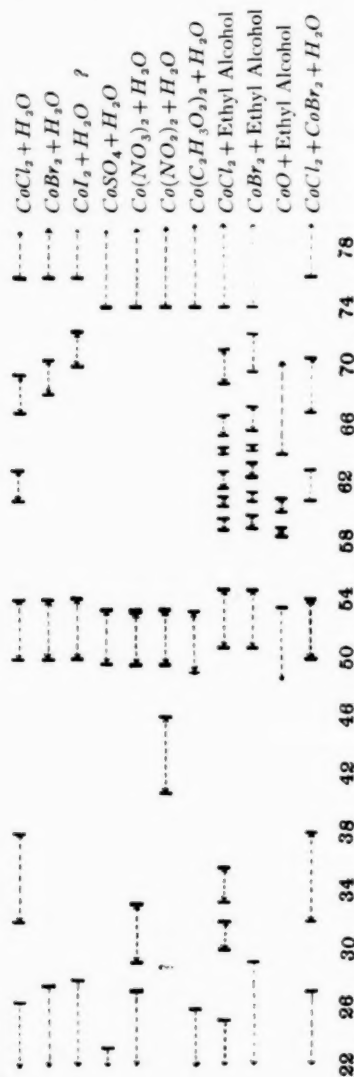


FIG. 1

If it were due to the cobalt kation, then, as stated by Jones and Anderson, the solutions which are strongly dissociated ought to show the

bands of much greater intensity than solutions which are less dissociated. This, however, was not the case, for the bromide and chloride, which are most dissociated, showed a much less intense absorption band in the green than did the acetate, sulphate, and nitrate, for the same concentration and length of absorbing layer.

The positions of the absorption bands in the red region of the spectrum were not the same for any two salts in aqueous solutions; but, on the other hand, some solutions had absorption bands in the red which are characteristic of that solution itself, while others, such as the nitrate, sulphate, and acetate, transmitted perfectly all the light as far as λ 7400. This shows that the "absorber" which produced the absorption in the red must be different for each solution, as we have already shown that the bands in the spectrum of a solution of cobalt chloride, for instance, were an entirely different set of bands from those in the spectrum of cobalt bromide. Moreover, the "absorber" which produced the absorption bands in the red must be different from that to which the band in the green is to be ascribed.

If we compare the spectrum of the aqueous solution of a salt with the spectrum of the same salt dissolved in ethyl or methyl alcohol we find that the position of the absorption bands was not the same. Moreover, the bands in the red region of the spectrum of an ethyl alcohol solution of cobalt chloride, for instance, always appeared first, and were always present even in very dilute solutions; the band in the green appearing only after the solution has become more concentrated. On the other hand, the band in the green region of the spectrum of an aqueous solution of cobalt chloride always appeared first, while the bands in the red could not be seen until the solution had become very concentrated. This is what we would expect if the absorption is produced by different kinds of "absorbers."

In the absolute ethyl alcohol solution there is very little dissociation, so we would obtain the spectrum of the undissociated molecule of cobalt chloride even in dilute solutions; while in the case of the more dilute water solutions there would be nearly complete dissociation and, therefore, the bands due to the molecule would not appear until the solution had become concentrated. Moreover, if the band in the green is due to the cobalt atom and not to the cobalt kation, then we would expect the intensity of this band to be roughly propor-

tional to the concentrations, as it was in the case of the solutions studied.

The most reasonable explanation of the fact that the absorption bands in the red region of the spectrum of an absolute ethyl alcohol solution of cobalt bromide, for instance, are not in the same position in the spectrum as the corresponding bands in an aqueous solution of the same salt, is that there is some "simple" hydrate of the molecule formed and that the "absorber" which produces these bands in the red is these "simple" hydrated molecules.

The spectrograms as represented in Fig. 1 show very clearly that the oxygen present in the molecule of the salt plays a very important rôle in its absorption, for in the case of cobalt nitrate and cobalt nitrite their only difference in composition is in the amount of oxygen in the radical which is combined with the cobalt atom.

RESULTS WITH COPPER SALTS

For most of the work with the solution of copper salts, the Rowland concave grating was used. Only aqueous solutions of copper salts were examined. The concentration of the solutions used was varied from 5.0 to 0.1 normal and the lengths of the absorbing layer were 1 cm, 2 cm, and 4 cm. The source of light for all the work with the concave grating was the arc with Norway iron for electrodes.

Copper chloride in water.—There was strong absorption in the blue, violet, and ultra-violet and also a strong band in the red. The absorption of the short wave-lengths was probably due to more than one band, as was evident both from the spectrograms and the visual observations made with the quartz spectrograph when using very dilute solutions. With greater concentration of the absorbing solution, however, the limit of transmission was about λ 4800, giving the appearance of a single absorption band.

In the red the edge of the absorption band was not so sharply defined as in the case of those in the violet and ultra-violet. This band appeared to move up from the infra-red, that is, became wider as the concentration of the solution was increased, and in more concentrated solutions there was complete absorption as far as λ 5900.

Copper nitrate in water.—The ultra-violet absorption in the case of copper nitrate did not extend so far toward the longer wave-lengths

as in the case of copper chloride. The limit of transmission in the case of the most concentrated solutions of copper nitrate was about λ 3550, while there was absorption as far as λ 4800 in the case of copper chloride. With very dilute solutions the absorption in the blue and violet could not be seen. The band at λ 3550 was probably due to NO_3 , while the absorption of the copper chloride in the blue and violet was evidently produced by the molecule of copper chloride, or to the molecule and whatever it was associated with, and not to the copper ions.

The absorption band in the red was in practically the same position as that in the case of copper chloride, showing that these bands were undoubtedly produced by the same kind of "absorber."

Copper acetate in water.—In the case of the concentrated solutions of copper acetate the limit of transmission in the shorter wave-

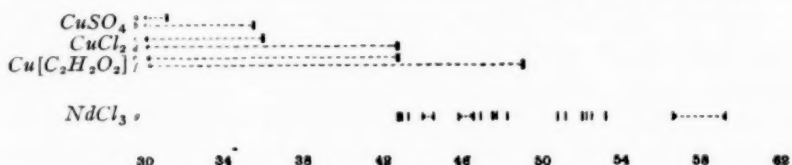


FIG. 2

lengths was farther toward the red than with either the copper chloride or nitrate, as is shown in Fig. 2. In Fig. 2, (c) and (d) represent the spectrum when the light was passed through a solution of copper chloride at different concentrations, while (e) and (f) give the spectrum when solutions of copper acetate of corresponding concentrations were used. It is evident that the absorption in this region of the spectrum must be ascribed to different "absorbers" in the case of the different salts.

The absorption band in the red was in about the same position as that of the chloride and nitrate.

Copper bromide in water.—For the work with copper bromide only very dilute solutions could be used, as there was too much general absorption with the solutions of greater concentration. The absorption bands with the bromide were similar to those of copper chloride, but they were displaced in position. With the more concentrated solutions the limit of transmission in the violet was λ 4525.

In the red the most concentrated solution transmitted everything as far as λ 6400, but when the solutions were less concentrated there was transmission as far as λ 7300.

Copper sulphate in water.—The solutions of copper sulphate showed less absorption in the violet and ultra-violet than did the other salts of copper, the limit of transmission being farther toward the ultra-violet. The red band, however, was in about the same position as in the case of the other salts of copper.

In Fig. 2, (a) and (b) represent the variation of the absorption as the concentration of the copper sulphate solution is increased. The concentration of these solutions was the same as that of the solutions of copper chloride and copper acetate, the absorption spectrum of which is also represented in Fig. 2.

Copper chlorate in water.—The work with copper chlorate was undertaken for the purpose of comparing its absorption with that of copper nitrate, the object being to have the composition of the salts the same except the chlorine and nitrogen.

With dilute solutions, the spectra of the solutions appeared about the same, but as the concentration of the solutions was increased, the color of the solutions differed more and more. This difference was less pronounced than in the case of cobalt nitrate and cobalt nitrite, where the only difference in composition of the salts was in the amount of oxygen that the salt contained. It is evident, however, that the chlorine and nitrogen play a rôle in the absorption of the salts in solution.

Results with copper salts.—By comparing the absorption spectra of the various solutions of copper salts we find that some of the bands are common, while there are others which are characteristic of each spectrum. This is what would be expected if there were two kinds of "absorbers," the one producing the red band being the copper itself, while the molecule would be responsible for the characteristic bands.

Moreover, since the color of the solutions of copper chlorate and copper nitrate was not the same for the same concentration of the solution, it is evident that the chlorine and nitrogen must play a rôle in the absorption.

Ferric chloride in water.—For the work with ferric chloride the

second method of investigation was employed, in which the spectrum was examined visually by means of the quartz spectrograph and the prism spectroscopes.

The method of carrying out this part of the work was similar to that used in the case of cobalt chloride: light from an iron arc and the Nernst filament were focused respectively upon the slit of the quartz spectrograph and the prism spectroscopes, by means of quartz condensing lenses, the light having passed through a cell 1 cm thick containing pure water. The ferric chloride was then slowly added to the water and the absorption bands examined. There appeared to be two regions of absorption, one in the extreme ultra-violet and another farther toward the red, extending from the ultra-violet into the violet and blue. These two bands appeared as one except when the violet band first became visible. The latter band, however, did not appear until the solution was quite concentrated.

The same experiment was repeated by adding the ferric chloride to dilute nitric acid. When this was done free chlorine was given off and the band in the ultra-violet and violet could not be seen. This is what would have happened if the absorption in the ultra-violet and violet had been produced by the combined iron and chlorine or by any "simple" hydrate of this salt.

Neodymium chloride in water.—The work with neodymium salts was not completed until after the paper by Jones and Anderson appeared.

The absorption spectrum of neodymium salts was examined both with the grating spectroscope and with the quartz spectrograph.

The spectrograms showed several strong absorption bands in the visible region of the spectrum, and also several others in the ultra-violet could be seen by means of the quartz spectrograph. There were also several bands in the red which were not shown on the spectrograms. In Fig. 2, (g) represents the absorption bands in the visible region of the spectrum of neodymium chloride, beginning with the broad band in the yellow and extending as far as the sharp narrow band at λ 4275. The band in the yellow extending from λ 5660 to λ 5930 was broken up into five narrow bands, but they were too faint to be well reproduced. Below is given a list of the bands which were measured.

λ	Character
4275.....	Strong and well defined
4290.....	Faint
4330.....	Broad, hazy
4405-4458.....	Broad, hazy
4590-4655.....	Edges hazy
4695.....	Quite sharply defined
4750-4768.....	Edges sharp
4820.....	Hazy
5090.....	Quite sharp
5120.....	Hazy
5205.....	Sharp
5221.....	Sharp
5252.....	Hazy
5320.....	Hazy
5660-5922.....	Sharp on violet side

The wave-length of the absorption bands in the ultra-violet region of the spectrum was not determined, as the spectra were examined with the quartz spectrograph and the bands were too faint to be determined. There were also several in the red which were not measured.

Neodymium bromide in water.—The absorption spectra of neodymium bromide was very similar to that of neodymium chloride, although the solutions were a much deeper red than those of the chloride. For corresponding concentrations, however, the bands of the bromide solutions were much more intense than for the neodymium chloride. The bands were apparently slightly displaced, but this slight displacement cannot be reproduced in the spectrograms.

Neodymium sulphate in water.—The spectra of the solutions of neodymium sulphate differ considerably from those of the solutions of neodymium chloride. This difference was not apparent, however, unless the spectra were examined carefully, and it was much more easily seen in the case of the more concentrated solutions. The bands in the spectra of the sulphate solutions were broader and more hazy than those of the solutions of neodymium chloride.

Neodymium salts in other solvents.—The spectra of neodymium chloride and bromide were also examined when these salts were dissolved in other solvents than water. Both of these salts were dissolved in each of the solutions of absolute ethyl alcohol, glycerine, and acetic acid, and the absorption spectra studied. This work,

however, has not been entirely completed. In each case the spectrum was found to differ from the corresponding spectrum when the salt was dissolved in some other solvent. Not only did the spectra of different salts differ from each other, but some of the bands which were intense when the salt was dissolved in one solvent were narrow and faint when this salt was dissolved in some other solvent.

SUMMARY

The conclusions which have been reached from this work may be stated briefly as follows:

1. The absorption of solutions of the salts which have been studied is due to different kinds of "absorbers," one of these, at least, being the molecule of the salt and another the atom.
2. The absorption spectra of these salts in solution depends to a great extent upon the solvent, which probably forms some "simple" hydrate.
3. Each constituent of the molecule of these salts plays some rôle in their absorption.

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A SIMPLE CRITERION FOR THE DETECTION OF ANOMALIES IN THE ORBITS OF SPECTRO- SCOPIC BINARIES

By D. F. COMSTOCK

It has often been remarked that discoveries are oftenest made through close examination of observed exceptions to well-known laws or wide generalizations. Anomalies in the field of stellar motion are as important as elsewhere, but when the moving stars constitute a spectroscopic binary it is not always very easy to find out whether the observed velocity-curve is explainable by simple motion of two bodies under the law of gravity or whether some disturbing cause must be sought.

In looking for a particular type of apparent anomaly which was to be expected on a theory of light-velocity to be discussed elsewhere, the author had occasion to study the problem of two bodies, with a view to obtaining, if possible, a simple relation which was characteristic merely of motion under gravity and independent of the constants of any particular orbit.

A relatively simple relation was found which is best stated in terms of the curve which is the integral of the common radial velocity-curve and which I will call the "distance-curve." The distance-curve is easily obtained by plotting as abscissae the times and as ordinates the *area* of the velocity-curve between zero velocity and the time-ordinate chosen. Thus if in Fig. 1 v is the velocity-curve, then d is an approximate representation of the distance-curve. If the axis OP is so chosen that the area of the v -curve above it is just equal to the area below, then the ordinates of the d -curve give the distance of the star at any instant from the nearest point of the orbit, this point being of course considered as moving with the center of gravity of the system.

The relation to be proved is then between the width of the distance-curve, such as MN , at any point and its height LM at the same point.

It may be written thus:

$$\frac{w}{W} = \frac{1}{\pi} \left\{ \cos^{-1} \left(2 \frac{h}{H} - 1 \right) - 2 \left(2 \frac{h_1}{H} - 1 \right) \sqrt{\frac{h}{H} \left(1 - \frac{h}{H} \right)} \right\} \quad (1)$$

where

h = height of distance-curve at any point;

w = width of distance-curve at same point;

h_1 = height of distance-curve at the abscissa corresponding to the maximum point of velocity-curve (KS , Fig. 1);

H = maximum height of distance-curve;

W = total width (i.e., length of base) of distance-curve.

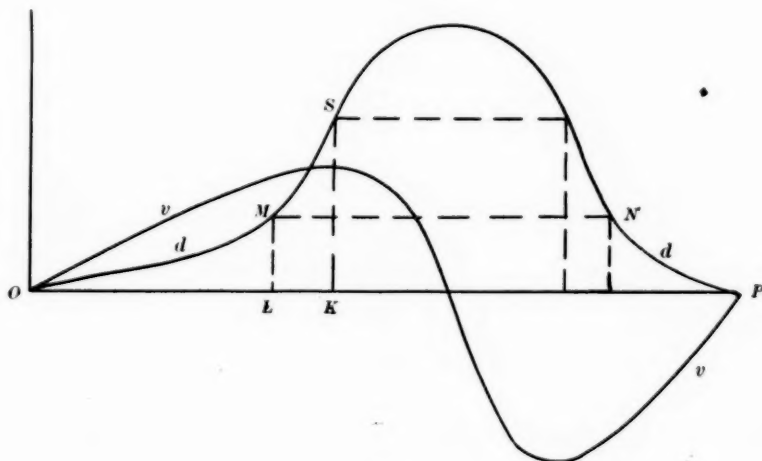


FIG. 1

PROOF OF RELATION

In order to prove equation (1) it will be convenient to state six theorems which are quite simple in themselves and on which this equation may be based.

Theorem I.—This is a geometrical theorem and states that if (Fig. 2) in any circle are drawn two parallel chords CB and MN , two tangents HRL and AVY parallel to these chords, and the diameter RV perpendicular to the tangent, and cutting the chords

in P and Z ; then if F is any point on the chord CB and the lines MF and FN are drawn, the following relation holds:

$$\frac{\text{Area } MFNBRCM}{\text{Total area of circle}} = \frac{1}{\pi} \left\{ \cos^{-1} \left(\frac{VZ}{D} - 1 \right) - 2 \left(\frac{VP}{D} - 1 \right) \sqrt{\frac{VZ}{D} \left(1 - \frac{VZ}{D} \right)} \right\} \quad (2)$$

where D is VR , the diameter of the circle.

This theorem can readily be proved by subtracting the area of $\triangle MFN$ from segment MRN .

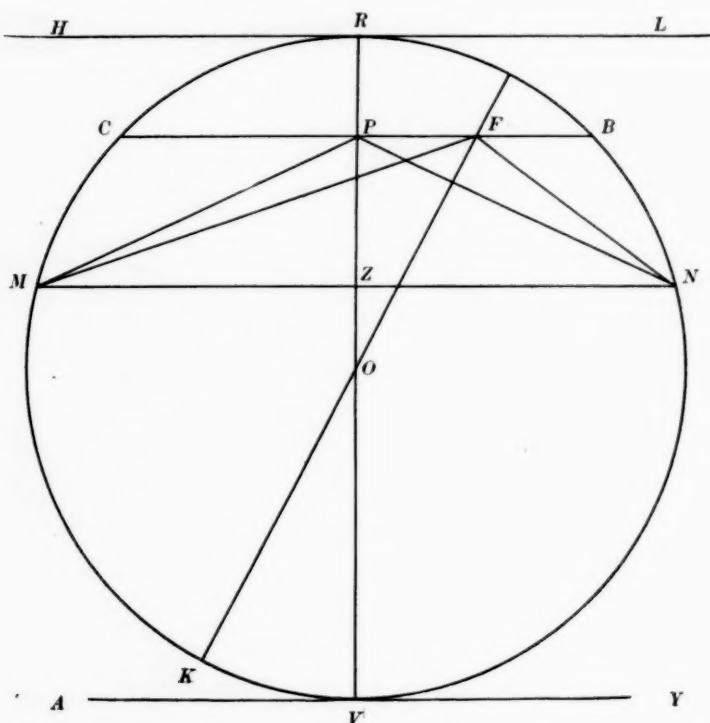


FIG. 2

Theorem II.—If four planes, each perpendicular to the line of sight, be imagined drawn in connection with the real orbit (Fig. 3), two tangent to the orbit, one through the focus, and one at any distance (z) from the nearest tangent plane, then the orbit, together

with the intersection of these planes with the plane of the orbit, may be completely represented by the projection of a certain circle similar to that of Fig. 2, with the various lines as there drawn.

This is readily seen to be true if the point F and the direction of the lines HL , CB , etc., are properly chosen on the circle of Fig. 2. For clearness Fig. 3 is lettered similarly to Fig. 2.

Theorem III.—The relation of Theorem I holds also for the ellipse of Fig. 3, if the corresponding letters are substituted. That is,

$$\frac{\text{Area } M'F'N'B'R'C'M'}{\text{Total area of ellipse}} = \frac{1}{\pi} \left\{ \cos^{-1} \left(2 \frac{V'Z'}{D'} - 1 \right) - 2 \left(2 \frac{V'P'}{D'} - 1 \right) \sqrt{\frac{V'Z'}{D'} \left(1 - \frac{V'Z'}{D'} \right)} \right\} \quad (3)$$

This follows from the fact that, since each area and line of Fig. 3 is a projection of the corresponding line or area of Fig. 2, we can write

$$\frac{\text{Area } M'F'N'B'R'C'M'}{\text{Total area of ellipse}} = \frac{\text{Area } MFNBRCM}{\text{Total area of circle}} \quad (4)$$

$$\frac{V'Z'}{D'} = \frac{VZ}{D} \quad (5)$$

$$\frac{V'P'}{D'} = \frac{VP}{D} \quad (6)$$

Theorem IV.—The ratio $\frac{V'Z'}{D}$ in the right-hand side of the relation of Theorem III may be found from an examination of the experimentally determined distance-curve of Fig. 1. In fact

$$\frac{V'Z'}{D'} = \frac{h}{H} \quad (7)$$

where h and H are the quantities in equation (1).

To prove this it is merely necessary to remember that the ordinates of the distance-curve (Fig. 1) give the distance of the body at any instant from the nearest tangent plane to the orbit. From this it is evident that h and H are simply projections of $V'Z'$ and D' on the line of sight.

Theorem V.—The ratio $\frac{V'P'}{D'}$ on the right of the relation in Theorem III may also be found from an examination of the experimentally determined distance-curve of Fig. 1. In fact

$$\frac{V'P'}{D'} = \frac{h_1}{H} \quad (8)$$

where h_1 and H are the quantities in equation (1).

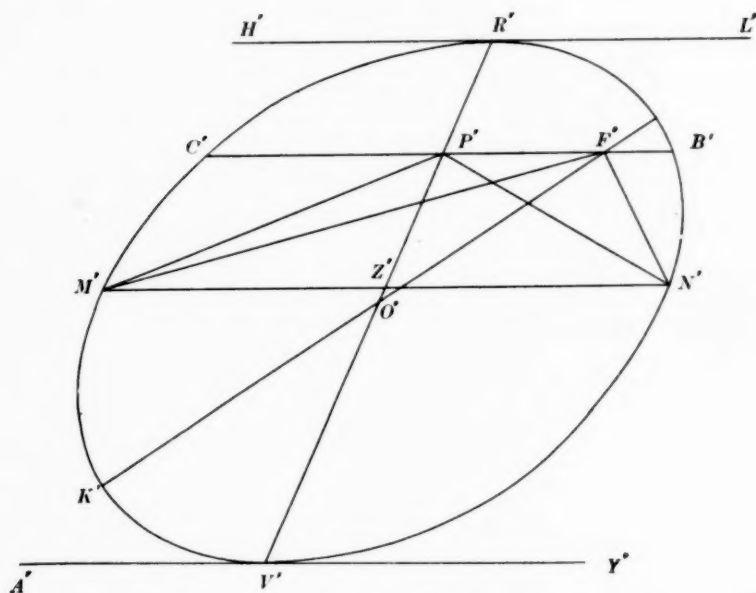


FIG. 3

This follows from the fact that h_1 was defined as the ordinate of the distance-curve which had the same abscissa as the maximum point of the radial velocity-curve. It follows, however, from the simplest expression of Newton's Laws as applied to central forces that the radial velocity is a maximum when the body is in a plane through the focus drawn perpendicular to the line of sight. Thus the height h_1 of the distance-curve represents the distance of the focus of the orbit from the nearest tangent plane.

Theorem VI.—The ratio which forms the *left*-hand side of the relation of Theorem III may be found from an examination of the experimentally determined distance-curve of Fig. 1. In fact

$$\frac{\text{Area } M'F'N'B'R'C'M'}{\text{Total area of ellipse}} = \frac{w}{W} \quad (9)$$

To prove this it is merely necessary to remember that from Kepler's Law the ratio

$$\frac{\text{Area } M'F'N'B'R'C'M'}{\text{Total area of ellipse}} \quad (10)$$

is equal to the time that it takes the body to go from M' to N' divided by the total time to go once around the orbit. By construction M' and N' are at equal distances from the nearest tangent plane and hence the positions M' and N' are represented by equal ordinates on the distance-curve. Hence the *width* of the distance-curve corresponding to the $M'N'$ ordinate, divided by the total width (the base) of the curve, is the time it takes the body to go from M' to N' divided by the periodic time and hence is equal to the above ratio (10).

It is evident that from Theorems IV, V, and VI the relation of equation (1) follows directly. We thus have

$$\frac{w}{W} = \frac{1}{\pi} \left\{ \cos^{-1} \left(2 \frac{h}{H} - 1 \right) - 2 \left(2 \frac{h}{H} - 1 \right) \sqrt{\frac{h}{H} \left(1 - \frac{h}{H} \right)} \right\} \quad (11)$$

SUMMARY AND CONCLUSION

The criterion for the detection of anomalies in the orbit of spectroscopic binaries which has been set up in this paper, may be outlined in words as follows:

If a plane be drawn through any simple double star orbit perpendicular to the line of sight, then the time during which one of the stars is on the far side of this plane is a simple function of the position of the plane along the line of sight, and of the position of the focus along the line of sight. All three of these quantities can be determined with great ease from the true radial-velocity-curve of one star.

If the time be expressed in terms of the periodic time, and the distance along the line of sight, measured from the nearest point of

the orbit, be expressed in terms of the total length of the projection of the orbit on the line of sight, then the equation contains *no constant of the orbit except the distance of the focus along the line of sight expressed in the same way.*

This criterion is uniquely suited for the detection of any apparent anomaly in the motion of binary stars due to a possible dependence of the velocity of light on the velocity of the source. It was developed solely for this reason and the author is now using it with the purpose of detecting such an effect, does it exist. It was thought, however, that, since the criterion is so general and the relation itself so simple, compared with the complexity of the integral function connecting velocity and time, it might be found useful in other problems than the one for which it was developed.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

March 4, 1910

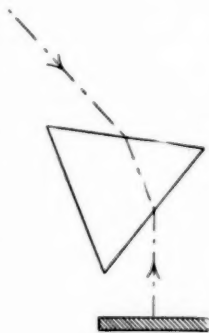
MINOR CONTRIBUTIONS AND NOTES

AN IMPROVED METHOD OF USING QUARTZ PRISMS

In all quartz spectrographs in which the optical train is composed of crystal quartz for work in the ultra-violet it has been found necessary to make the dispersing prism of two halves, one of right and the other of left-handed quartz, to eliminate the doubling of the spectrum lines due to the two oppositely polarized circular vibrations.

This trouble may be overcome in another way, which is at the same time simpler, cheaper, and makes a gain in defining power.

A solid 60° quartz prism was constructed by Hilger of London with the axis of the prism running parallel to its base. This prism is mounted in an instrument of the Littrow type with an object-glass of about 90 inches focus. Behind the prism is mounted a metal reflector so that the light passes through the prism on to the mirror and is reflected back through the prism and along its original path (see diagram). If now the image of the slit be examined, it will be found that the doubling effect is entirely eliminated.



This prism was replaced by a Cornu prism of the same size, but no difference could be detected except that the solid prism gave better definition, due probably to the fact that four surfaces had to be worked on the Cornu prism instead of two on the solid one.

I must say, however, that it is extremely important that the optic axis of the prism should run parallel to the base or it will be found necessary to turn the prism slightly out of minimum deviation to get the single image. I have not heard of a solid quartz prism being used in this way before but it is quite possible that it has been. If so, I should be glad to hear of it.

Of course, a 30° prism can be used in a similar way.

F. STANLEY

THE LABORATORY, ADAM HILGER, LTD.

LONDON

January 21, 1910

DETERMINATION OF ABSOLUTE WAVE-LENGTHS WITH OBJECTIVE-PRISMS¹

Nearly all of the photographs of stellar spectra, made by the aid of the Henry Draper Memorial, have been taken with objective-prisms. The principal objection to this method of photographing the spectra of stars has been that it does not provide the means of determining their velocities in the line of sight. Various methods of remedying this difficulty have been tried here, and were described in 1891, in *H.A.*, 26, chap. xxi. Among these methods are absorption by didymium and hyponitric acid, variation in length of a known portion of the spectrum, and the use of an auxiliary prism. The first of these methods appeared to be the simplest and best, but the absorption bands were too wide and hazy for precise measurement. The second method was then shown to be impracticable, but has since been recommended by Orbinskij, and is commonly ascribed to him. Another method, turning the prism 180° , was proposed in *H.C.* 110, and is now generally regarded as the best method yet proposed.

After discussing this problem with Professor Robert W. Wood of Baltimore, at my request, he prepared the following statement:

¹ My attention was drawn recently by Professor E. C. Pickering to the great need of a ray-filter giving one or more sharp and narrow absorption lines, for the determination of stellar velocities with the objective-prism.

It occurred to me that the 4272 band of neodymium might answer the purpose. In a solution of the double nitrate of neodymium and ammonium (now procurable in large quantities as a by-product in the manufacture of Welsbach mantles) I found that the band was much too wide for use in the determination of stellar velocities. The solution of the pure chloride, however, was quite different, for the band was found to have contracted to a width of less than three Ångström units

EDITORIAL NOTE.—The pressure upon the space in this *Journal* during recent volumes made necessary the adoption of a general rule favoring priority of space to articles which would not be published elsewhere in English. This unfortunately has made it impossible for the Editors to bring before the readers of this *Journal* many valuable circulars and bulletins upon astrophysical topics, issued from various observatories, such as could formerly be reprinted in these pages. The managing editor of course reserves to himself some elasticity in the application of such a general rule, and he is glad to find space for this circular by Professor Pickering, which records such a decided step of progress in the more precise quantitative utilization of plates taken with the objective-prism.

E. B. F.

¹ *Harvard College Observatory Circular* 154.

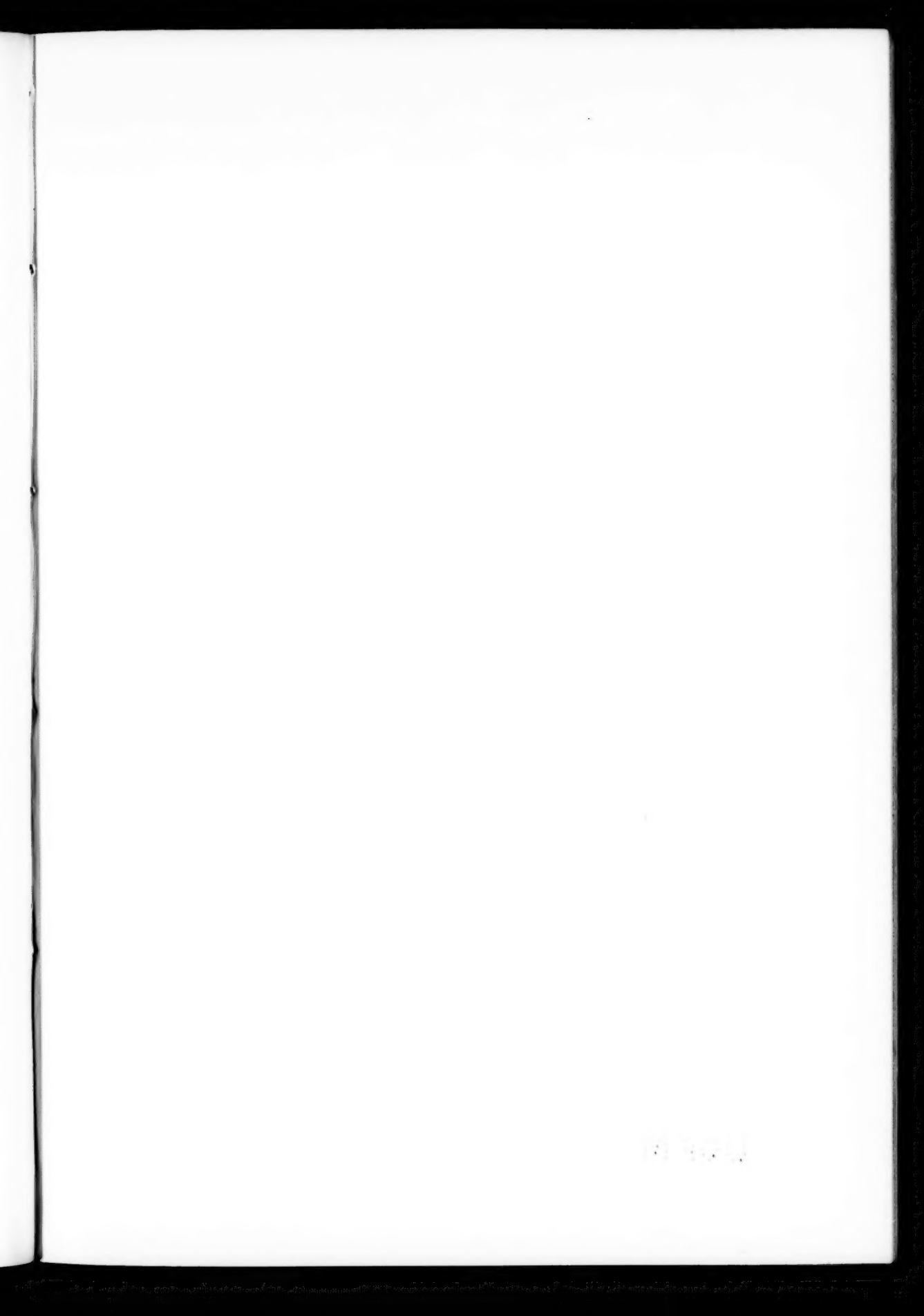


PLATE X



FIG. 1.—Spectra with Grating (R. W. Wood)

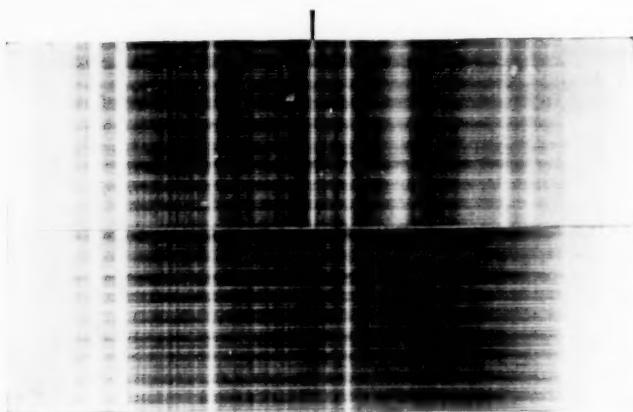


FIG. 2.— α *Canis Minoris*

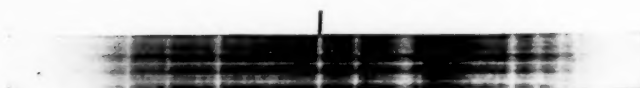


FIG. 3.— ϕ^1 *Orionis*

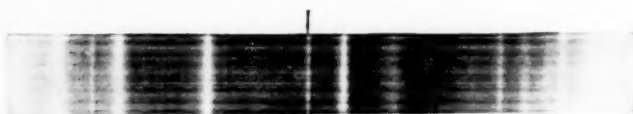


FIG. 4.— β *Aurigae*



FIG. 5.— β *Orionis*

STELLAR SPECTRA WITH ABSORPTION LINE OF NEODYMIUM CHLORIDE

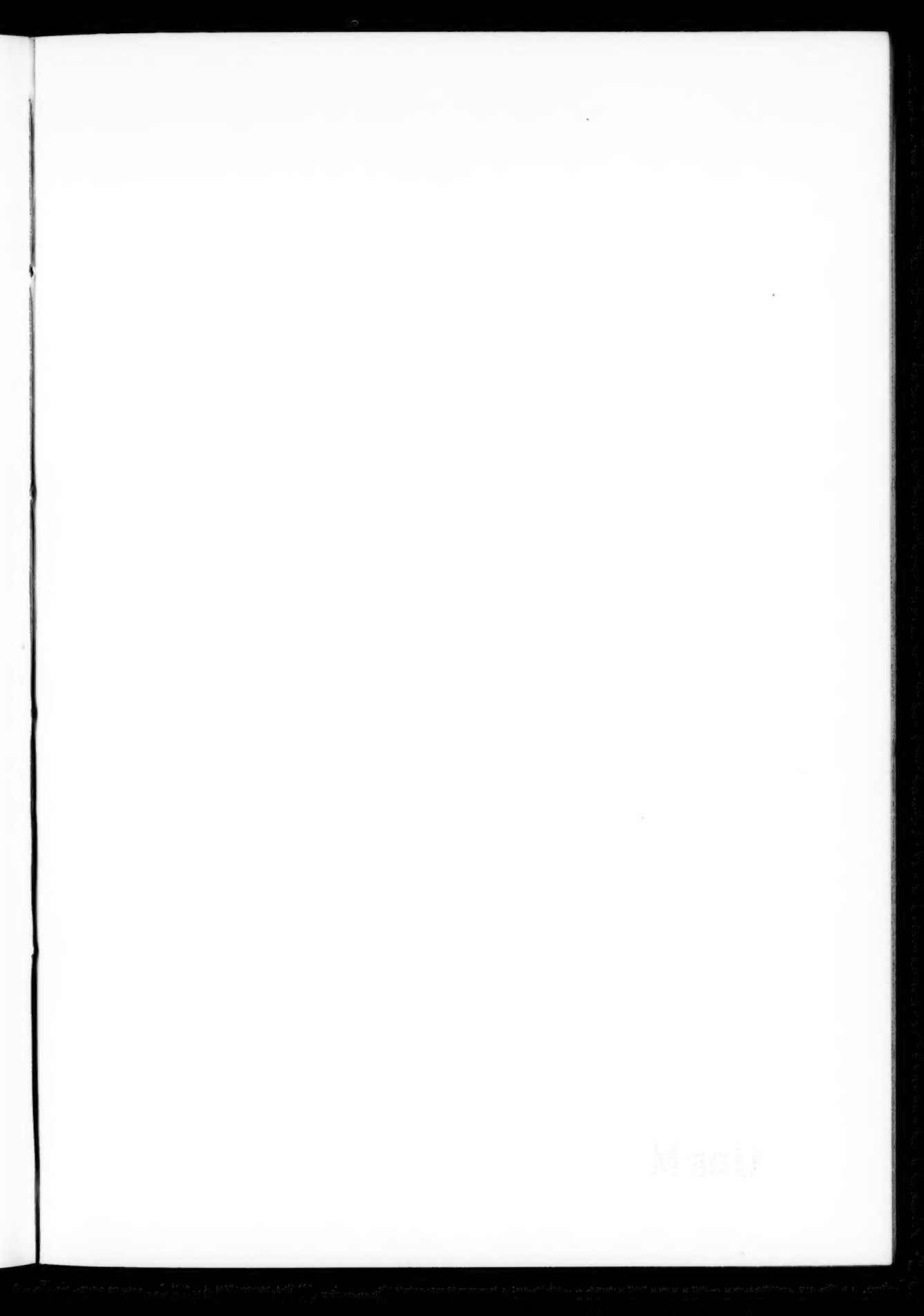
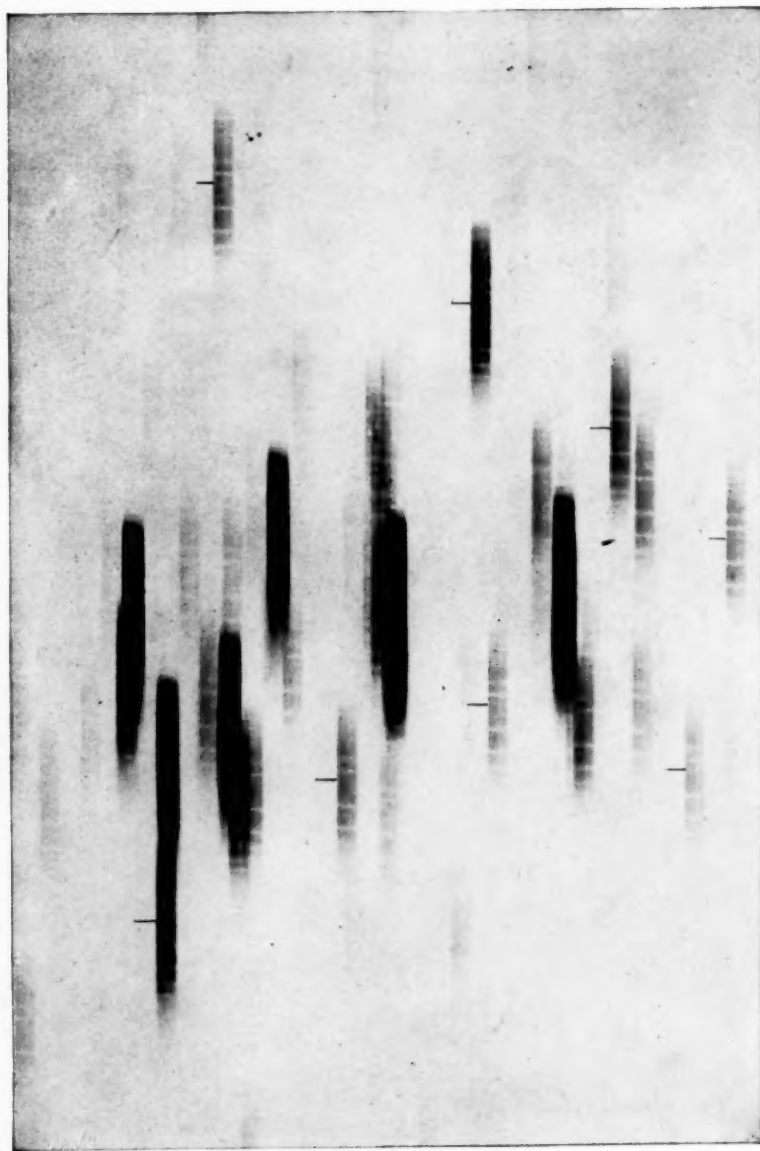


PLATE XI



SPECTRA OF THE *Plades*, WITH NEODYMIUM COMPARISON LINE

and its center could easily be determined to within 0.15 \AA.U. The absorption spectrum was photographed with a concave grating of 7 feet radius, together with the iron spectrum, and it was found that wave-length determinations referred to the neodymium line could be determined certainly to within 0.10 \AA.U. This would enable stellar velocities to be determined to within less than 10 kilometers per second. The strength of the solution must be regulated according to the thickness of the cell. For a cell 4 mm in thickness I diluted a saturated solution with about five parts of distilled water. It is very easy to determine the proper strength by trial. It may be possible to still further contract the band by the addition of some other substance. It has been found that lanthanum increases the sharpness of some of the didymium bands, also phosphoric acid. Experiments in this direction are in progress. The photograph of the absorption line with a rough scale of wave-lengths and the iron spectrum is reproduced in Fig. 1 (Plate X). The absorption line is almost in coincidence with the close double line of iron at wave-length 4271.5.

Professor Wood has also kindly filled a ray-filter with the solution named above, and a number of stellar spectra have been photographed through it.¹ Plate XI represents a photograph of the *Pleiades* taken with the 8-inch Draper telescope, on February 14, 1910, exposure 54 m., enlarged 2.72 times. The other spectra were photographed with the 11-inch Draper telescope, and were enlarged 1.56 times. The lengths of exposure are those of the portion of the photograph shown in the plate. On Plate X Fig. 2 represents the spectrum of α *Canis Minoris* taken with and without the cell interposed, on February 18, 1910, each exposure being 21 m. Fig. 3 represents the spectrum of *H.R.*, 1876, ϕ^1 *Orionis*, taken February 18 with an exposure of 55 m. Fig. 4 represents the spectrum of *H.R.*, 2088, β *Aurigae*, taken February 19, 1910, with an exposure of 17 m. This star is a spectroscopic binary and the stellar lines have become double, as may be seen in line K in the original negative. The neodymium line of course remains single. Fig. 5 represents the spectrum of *H.R.*, 1713, β *Orionis*, taken February 19, 1910, with an exposure of 8 m.

It will be seen from Plate XI that a large number of spectra may be photographed on a single plate, with sufficient distinctness to enable the lines to be measured with accuracy. This is also shown in *H.A.*, 26, Plate VII. Several absorption bands are shown in Fig. 3, but only one, λ 4272, is sufficiently well defined to be satisfactorily meas-

¹ When placed just in front of the photographic plate.—EDS.

ured. It occurs in a very convenient place, in the brightest part of the spectrum, between the lines $H\delta$ and $H\gamma$. It is marked by a black line on several of the spectra. The lines in the spectrum of β Orionis, Fig. 5, are well defined, and can be measured with accuracy. It will be seen that the neodymium line appears to be at least as sharp as the hydrogen lines in this star, or as the calcium line, K.

The determination of the approximate motion of stars in the line of sight in this way becomes very simple. It is only necessary to measure the distance of the neodymium line, λ 4272, from $H\delta$, λ 4101, and $H\gamma$, λ 4340, and perhaps from some of the other lines, and then to derive their wave-lengths, by Hartmann's formula, assuming the neodymium line to be constant. The actual determination with sufficient accuracy to render this method of value, however, is a very different matter. While it is not probable that it can compete with the slit-spectroscope in determining the motions of the brighter stars, it may be worth while to compare the advantages of each, and thus see how far the new method may be useful in supplementing the old. This cannot be decided until this method receives the same careful study which has been made of the slit-spectroscope.

The principal objections to the slit-spectroscope are, first, the great loss of light. It is maintained that less than 1 per cent of the entire light falls upon the sensitive plate. Accordingly, only the brightest stars can be measured with accuracy, and even for these it is necessary to use the largest telescopes yet constructed. A second objection is the great rigidity required, and the necessity of maintaining a perfectly uniform temperature. The simplicity of the method of the objective-prism renders it probable that the sources of error are few in number, and therefore readily corrected. The loss of light is small, so that very faint spectra can be photographed. The principal work so far done with the slit-spectroscope has been with stars of the fifth magnitude and brighter.

In the *Harvard Circulars* announcing peculiar spectra it will be noticed that many of the stars are not contained in either the northern or the southern *Durchmusterung*, and must therefore be fainter than the tenth magnitude. These spectra, however, have well-marked bands or bright lines, which are easily seen. From the classification of the spectra of stars in clusters given in *H.A.*, 26, chap. xiv, it does

not seem unreasonable to expect that the spectra of stars of the first type as faint as the ninth magnitude can be photographed with sufficient detail to determine the approximate approach and recession. Plate VII of *H.A.*, 26, is an example of a plate taken with an objective-prism. The distance between the lines $H\delta$ and $H\gamma$ is here about 1.6 mm. On this scale 1 Ångström unit would equal 1".2, corresponding to 75 km. An error of $\pm 0".1$ would therefore represent ± 6 km. Preliminary measures of the three lines in the spectra of five stars photographed with the 11-inch Draper telescope gave a probable error of 10, 7, and 11 km for the mean of five settings on the lines $\lambda\lambda$ 4101, 4272, and 4340, respectively. It will be noticed that the error in the case of the neodymium line is distinctly less than those of the hydrogen lines. The only lines that can be photographed in faint stars whose spectra are of the first type are those of hydrogen. As they are wider than the neodymium line, this limits the accuracy with which such stars can be measured. Spectra of the second or third type must be much brighter to show measurable lines, but when these are visible, greater accuracy may be expected. The agreement of the various estimates given above renders it probable that, with our present means, we can determine the motion of a ninth-magnitude star of the first type with an error of about 10 km, and of an eighth-magnitude star of the second type with somewhat greater accuracy. Much wider spectra are needed to classify spectra than to measure the position of the lines. Unfortunately, when objective-prisms are used, if long exposures are made, producing narrow spectra, the definition is poor.

The Henry Draper Memorial has furnished the Harvard Observatory with excellent means for photographing stellar spectra with objective-prisms. At Cambridge, prisms are available for covering the mirrors or objectives of the following instruments: 24-inch reflector, interval $H\delta$ to $H\gamma$, 0.5 mm, scale $60'' = 1$ mm; 16-inch Metcalf telescope (doublet), prism under construction; 11-inch Draper telescope, two prisms giving intervals 5.5 and 11.5 mm, scale $54'' = 1$ mm; 8-inch Draper (doublet), two prisms giving intervals 0.0 to 1.7 mm, scale $162'' = 1$ mm. At Arequipa, 24-inch Bruce telescope (doublet), interval 1.7 mm, scale $60'' = 1$ mm; 13-inch Boyden telescope, two prisms, intervals 7.3 and 13.9 mm, scale

42" = 1 mm; 8-inch Bache telescope, two prisms, intervals 1.7 and 0.6 mm, scale 178" = 1 mm.

With this equipment, the Harvard Observatory is prepared to take such photographs as may be desired, and it invites the aid of astronomers experienced in measurements in the line of sight.

EDWARD C. PICKERING

DETERMINATION OF STELLAR VELOCITIES WITH THE OBJECTIVE-PRISM

My attention was drawn by Professor E. C. Pickering to the great need of a ray-filter giving sharp and very narrow absorption bands, for the determination of line-of-sight velocities with the objective-prism. Having used solutions of salts of the rare earths, neodymium and praseodymium, for the isolation of spectral lines in my work upon the fluorescence of sodium vapor, it occurred to me that the fine absorption lines of these substances might meet the requirements. The excellent results which Professor Pickering has already obtained with a small cell, which I filled with a solution of neodymium chloride, makes it seem well worth while to improve the method in every possible way. I found that the absorption band at λ 4273, by proper adjustment of the concentration, should enable us to determine velocities to within about 10 km per second, provided that the definition given by the prism was sufficiently good to admit of measurement to this degree of accuracy.

By the addition of erbium chloride we can get another good reference line at λ 382, and if we use an isochromatic plate, there is a double band (neodymium) at λ 5220, the bright central band of which is not over five or six Ångströms in width. With vapors, however, I feel sure that even better results can be obtained. I have examined a number already: perchloride of manganese gives groups of lines in the green resembling the *b* group in the solar spectrum, with low dispersion. There should be no trouble with the absorption part of the problem, for we can without doubt get numerous lines as fine as the prism and the atmospheric conditions permit of our resolving.

With the temperature of the prism accurately controlled, and "good seeing" conditions, I feel sure that the accuracy of the measurements can be greatly increased. It may be possible to find some salt of

neodymium which is superior to the chloride. The appearance of the band is quite different in the different salts. In the double salt with ammonium, in which form the salt comes as a by-product in the manufacture of Welsbach mantles, the band is very broad and diffuse. In the nitrate it is double, the two components being of very unequal intensity, and not quite as sharp as in the chloride. Other salts are in process of preparation.

Anderson's work has shown that water is probably the best solvent. In alcohol the $\lambda 4273$ line disappears entirely and two new lines, much wider and fainter, appear a little on the red side of it.

I have not yet tried solvents which become solid, but shall do so shortly. If it is possible to get it into solution in styrol, we may be able to make a solid screen, for by keeping styrol at a temperature of 100° for a day or two it is converted into a hard, glassy substance (metastyrol) which has the same refractive index as flint glass, and is insoluble in water, acids, and most organic solvents.

I used this substance twelve years ago for the preparation of solid masses which would show the Christiansen colors, mixing powdered glass with styrol and then converting it into metastyrol (see *Physical Optics*, p. 92).

R. W. WOOD

BALTIMORE
April 4, 1910

NOTE ON THE ACCURACY OF RADIAL VELOCITY DETERMINATIONS

There has been of late some tendency, particularly on the part of writers who have not had opportunity to make or measure spectrograms, to exaggerate the accuracy of determinations of radial velocities with the best modern spectrographs. The statement is sometimes seen that the precision has now reached the tenth of the kilometer.

It seems to me only proper that a word of caution should be expressed at this time in order to avoid misunderstandings on the part of astronomers and physicists who have not had direct experience in this particular line of work.

A conservative point of view might succinctly be stated by raising the question whether we today know the radial velocity of any star in the heavens to the nearest kilometer.

Measurements of the same plate (obtained with good, high-dispersion spectrographs) by two different but equally experienced observers may yield results, based upon a dozen well-chosen lines, which differ in the mean by a whole kilometer, or even more. Where the process involves different instruments, observers, and sources of comparison spectrum, as well as different methods of measurement and reduction, the discrepancies may be of the order of two or more kilometers. It is highly desirable that all such elements should be as different as may be feasible, in order that from a comparative study of the results for the same star at different institutions, some idea of the systematic errors may be gained and a closer approximation to the true radial velocity be obtained. It was from this point of view that I suggested several years ago that certain standard stars should be observed with some regularity at different observatories. A large number of such spectrograms have been made here and at several other institutions. When these are all fully reduced and published, valuable data will be at hand for a study of present-day precision in line-of-sight work.

Without wishing to push too far the somewhat radical query above expressed, let us for a moment examine the case of *Arcturus*, a bright star involving only a short exposure with powerful spectrographs, whereby changes of temperature and of flexure are largely avoided. Its lines are sharp and the spectrum does not differ enough from that of the sun to involve many differences of blending of the lines. Results have also been published for this star by numerous observers, and it was very successfully employed by Professor Küstner for a determination of the solar parallax from the inferred radial velocity of the earth in its orbit. It was also included in the similar determination, more elaborately made at the Cape Observatory and recently published.¹

The table shows some of the recent values, readily accessible at this time.

Unfortunately no values have yet been published for this star by the Lick Observatory, nor have results with the high-dispersion spectrograph recently installed at Paris by M. Hamy been announced.

An examination of this list will probably convince the reader that

¹ *Annals of the Cape Observatory*, 10, Part 3, 1909.

for this exceptionally well observed star the radial velocity lies between -4.5 and -5.0 km, particularly in view of the large weight to be assigned to the last determination, made at the Cape. One might question the use of the thousandth of a kilometer in expressing the value for each plate, as has been done throughout the longer series at the Cape, inasmuch as their values for this star from plates taken consecutively on the same night in some instances differ by 1.5 km.

RADIAL VELOCITY OF *Arcturus*

Epoch	Observers	Number of Plates	Velocity	Extreme Range
			km	km
1902.3	Frost and Adams	8	-4.3	2.1
1902.4	Newall	6	-5.8	2.7
1902.4	Lord	7	-3.7	3.2
1903.1	Frost and Adams	5	-4.8	1.3
1903.3	Newall	19	-6.6	4.5
1903.4	Belopolsky	9	-6.1	3.3
1904.4	Belopolsky	18	-5.4	2.6
1904.8	Küstner	18	-4.8	1.2
1905.3	Plaskett	11	-4.6	2.3
1905.6	Slipher	5	-4.7	1.5
1907.00	Halm*, Cape	46	-4.7	4.9
1907.15	Halm†, Cape	55	-4.9	2.9

* Measured with ordinary machine.

† Measured with Hattmann spectrocomparator.

In thus commenting on these results at the Cape, I desire to express my high opinion of them, and would cite them as representative of high-grade spectrographic work: they illustrate my point that such differences do occur with the best modern installations. Granting, then, that a single plate of a star having excellent lines may yield results uncertain by one or two kilometers, it is evident that with low-dispersion, one-prism instruments, generally having a dispersion of one-third or one-fourth that just under discussion, three or four times that uncertainty may exist in regard to a single plate. Now, one-prism instruments are, moreover, much more liable to flexure than the three-prism form, whence additional uncertainty arises. In many spectra of the first type, which are often better investigated with low dispersion, the lines are so broad and ill-defined that large additional errors may be introduced, some of a systematic nature. It is a fact that it is sometimes necessary, in forming a mean, to combine values for separate lines which differ by as much as 30 km. Accordingly

we may hardly expect from such stars a value reliable within less than 5 km from a single plate, and the uncertainty may sometimes be twice this.

I have thus called attention to the unreliability of determinations of radial velocity in order to bring out more clearly the danger of overestimating the present possibilities of determining radial velocities with the objective-prism, in spite of the excellent progress recorded in Professor Pickering's circular elsewhere in this number (p. 372).

The simplicity and efficiency of the instrument have been recognized since the days of Fraunhofer, and the campaign conducted with it, using dry plates, under Professor Pickering's direction has yielded results of inestimable value, necessarily largely qualitative. As he states, however, the development of the instrument has not received the minute attention given to the slit-spectrograph, and this is doubtless because of the lack of reference points in the spectrum to serve as the basis for rigorous measurements. As further study is given to the production of ray-filters yielding absorption lines where needed throughout the spectrum, to the maintenance of the prism or prisms at a constant temperature during the night's work, and to the prevention of flexures of the mechanical and optical parts, it is, therefore, highly probable that a great gain in accuracy will be made in the near future.

Fully sharing Professor Pickering's views as to the difference between the statement of the method and the actual determinations by it, as clearly put forward by him (p. 374), I regret that I must be pessimistic as to his estimate (p. 375) that it is "probable that, with our present means, we can determine the motion of a ninth-magnitude star of the first type with an error of about 10 km, and of an eighth-magnitude star of the second type with somewhat greater accuracy."

Most spectrographers would reject without measurement any plate on which by some mischance only a single comparison line could be utilized. Even if three good comparison lines were available, at the middle and extremities of the spectrum, so that a satisfactory Hartmann formula could be calculated for the plate, it would still be quite beyond the usual practice to make the displacement of a star line depend upon a comparison line distant more than a few tenth-

meters, a linear distance ordinarily of much less than a millimeter. Without this safeguard of comparison lines, the effects of optical distortions, lack of uniformity of the film and glass surface, etc., would greatly increase the range of error of a plate.

Further, in the slit-spectrograph every effort is made to have the star's rays traverse the optical system centrally, which must diminish errors. One of the great advantages of the objective-prism is that it secures many spectra on one plate. This involves much distortion for stars away from the center of the plate, so that the scale-values, (Ångström units per millimeter) would vary decidedly over the plate, and depart capriciously from the normal values for the central rays passing the prism at minimum deviation.

The small scale given by most of the objective-prism telescopes listed as available at Harvard—and these are among the largest in use anywhere—also operates to diminish the accuracy of the determinations. None of the one-prism combinations gives a linear separation between $H\delta$ and $H\gamma$ equal, for instance, to that of the Bruce spectrograph of the Yerkes Observatory as arranged for one prism (10.5 mm), and only the two-prism arrangement of the 11-inch Draper telescope at Cambridge (11.5 mm) and the 13-inch Boyden telescope (13.9 mm from $H\delta$ to $H\gamma$) exceed its scale.

For such reasons as these it seems to the writer very doubtful that values "*with our present means*" more accurate than about 25 km per second are likely to be secured.

The question is, however, largely academic: it can be tested practically by measurements on the Harvard spectra provided with the neodymium line which have elsewhere been measured with slit-spectrographs.

With the highest appreciation of the splendid advantages of the objective-prism for radial velocity work when it has been sufficiently developed and when new filters are provided yielding many comparison lines well distributed throughout the spectrum, it seems to the writer that we should not allow ourselves to overestimate the precision at present attained, if this shall in any way diminish efforts and experiments to further improve this highly promising method.

EDWIN B. FROST

YERKES OBSERVATORY

REVIEWS

Atlas Stellarum Variabilium. Series VI, supplementing Series I, II, and III. By J. G. HAGEN. Berlin: Felix L. Dames, 1908. Pp. circa 70 and 63 charts. M. 92.

Series VI of this well-known atlas contains sixty-three charts of the fields surrounding sixty-five telescopic variables (*Z* and *RU Tauri* being on the same chart, also *Y* and *RS Pegasi*), with the corresponding catalogue sheets. The former series have proved so valuable that praise is superfluous, but it may be said that the present series is a distinct improvement over its predecessors, as the catalogue sheets contain a column of photometric magnitudes from the Harvard measures.

This series has been reviewed in various journals, but not from the standpoint of the faint stars in the vicinity of the variable. The reviewer has been engaged for the past two years, at the request of Father Hagen, in bringing out photographic prints on a scale of 10" to the millimeter, of all of the *Atlas* fields in which the variable becomes as faint at minimum as magnitude 13. The prints are about one-half degree square, and are from negatives taken with the 2-foot Yerkes reflector, showing stars to about magnitude 16.

As these prints will be used for identifying the variables when near minimum, it was necessary to compare carefully the print with the chart, and check the identification of the variable on each by the configuration of the surrounding stars. The variables were very faint on many of the photographs, hence it is no reflection on the charts to say that it was not always possible to identify the variable with certainty on the photograph, as there were frequently several faint stars near the place, any one of which might be the variable. It became necessary, therefore, to find the limits of accuracy of the charts and catalogue, in order to limit the area within which the variable might be situated. For this reason particular attention was paid to the stars in a square 5' each way from the variable, and any differences between the chart and the photograph, which might change the appearance of the group, were noted and measured.

Of the 63 fields in the series, 54 were photographed, and differences large enough to be noticeable were found on 28. As might be expected from the method of charting, the differences were nearly all in declination, the declination being read on a glass scale in the ocular of the Georgetown 12-inch refractor. It was found that differences as small as 0'.3 would not be noticed unless the configuration were especially favorable,

the actual range among the 24 differences of declination being from $0'.3$ to $1'.6$, the average being $0'.7$. This leads to the conclusion that in cases of doubtful identity, any star within $1'$ of the calculated place may be the variable, but if the distance be greater than $1'$, it is probably not the variable.

The list of differences thus found has been communicated to the author, who has announced his intention of publishing a list of corrections to the *Atlas*. It may be well, however, to mention here that Hagen's identification of the variable 7619 *RR Aquarii* differs from that given by Professor Abetti, the discoverer, who kindly marked a print sent to him, giving Hagen's No. 35 as the variable, $30''$ north preceding the star marked by Hagen. Abetti's observations of this star are given in the *Arcetri* publications, No. 12, p. 21, 1900.

It should also be mentioned that the variable 2376 *S Lynceis* has a companion, of just about its minimum brightness, distant $12''.5$ in position angle 155° . This is not mentioned in Hagen's work, and might easily be mistaken for the variable in its faint stages.

The only prominent star missing from the charts is one of magnitude about 10.8 near 5405 *RT Librae*, co-ordinates $-0^m 32^s$, and $-1'.0$. This star is not visible on the Harvard "Chart of the Entire Sky," Nos. 41 and 42, the limit of the plates being about ninth magnitude, near the corner of the plates.

Rather unexpectedly, the comparison of chart and photograph has been seldom affected by red stars of consequently faint photographic magnitude. The greatest difficulty encountered in this work has been that of finding the catalogue number of a given chart star, since the catalogue is arranged in order of brightness, instead of right ascension.

The photographic prints of 140 Hagen fields are now available, being for sale by the University of Chicago Press at cost, namely, 20 cents per sheet.

J. A. PARKHURST

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The Moon in Modern Astronomy. By PHILIP FAUTH. Translated from the German by JOSEPH McCABE, with an introduction by J. ELLARD GORE. New York: D. Van Nostrand Co., 1909. 8vo, pp. 160, with 66 illustrations. Price \$2.00 net.

This is an American reprint, from the original plates of the London edition issued a year previously, which was reviewed in this *Journal*, 29, 91, January 1909. Nothing needs to be added to that review.

Zur Geschichte der astronomischen Messwerkzeuge von Purbach bis Reichenbach, 1450 bis 1830. By JOH. A. REPSOLD. Leipzig: W. Engelmann, 1908. Pp. viii+132, with 171 illustrations. M. 16; bound, M. 18.50.

This volume contains a most interesting collection of plates illustrating the gradual development of those mechanical contrivances by means of which astronomers have observed the heavenly bodies during the last four centuries. Accompanying the plates is an explanatory text characterized by the two very desirable qualities of brevity and completeness. The author has consulted original sources whenever possible; and it is almost unnecessary to add that the plates and press work are of the high quality to be expected in an astronomical publication coming from the house of Engelmann.

One might perhaps suppose that a work of this kind would be of interest to those only who possess the curiosity of the antiquarian—who desire to compare the supposed excellence of our present age with the feeble attempts made by men of old. But a careful examination of the book has inclined the present reviewer to the opinion that active practical astronomers and makers of modern instruments might not improbably derive ideas of value from a study of the plates. And certainly the whole body of astronomical teachers will find an invaluable source of lecture material. Descriptive teaching is given life by sketching the manner in which the earlier investigators solved their problems. Too keen an insistence on elaborate descriptions of the very latest advances is apt to obliterate both the relatively greater importance of older discoveries and the high inherent interest of astronomy as a disciplinary study. We know vastly more about the sun-spots than Galileo knew; but our added knowledge might be summarized easily within the limits of a single printed page. It is good to see the old masters receiving a little effective advertising in Repsold's book.

Many teachers will perhaps be surprised to learn that Galileo invented a clock-escapement: his apparatus was not merely a simple swinging weight suspended by a string. The book contains a good picture of the complete apparatus. There are also several valuable plates reproduced from the *Machina Coelestis*, showing Hevelius observing with his great sextant of 1659. In these pictures a lady appears, taking as complete a share in the observing as Hevelius himself. In more recent work, such as that of Fraunhofer and Reichenbach, the book is of course very complete; in fact, we recommend it strongly to the attention of all astronomical teachers.

H. J.